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**MODERN ADVANCES
IN
INORGANIC CHEMISTRY**

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INORGANIC CHEMISTRY

BY
E. B. MAXTED

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PREFACE

MANY of the general observations which might logically form a preface have, for continuity, purposely been relegated to the first few paragraphs of the introductory chapter; and it accordingly seems sufficient here to summarize briefly the scope of the volume.

The subject-matter will be seen to fall into three main sections. In the first place an attempt has been made to present in an elementary and, it is hoped, easily readable manner an outline of the newer physical background to inorganic chemistry. Secondly, some modern advances in a few selected fields and the systematic chemistry of three recently discovered elements (hafnium, masurium, and rhenium) have been dealt with in greater detail. A short chapter on reactions in discharge tubes forms a bridge between classical inorganic chemistry and the newer nuclear chemistry. In this third section an account, which is necessarily rather superficial by reason of the infancy of the subject, has been given of nuclear reactions generally, including the preparation, properties, and uses of artificial radioelements and the extension of the normal periodic system by the successful preparation of transuranic elements.

In addition to the original papers referred to in the footnotes, I am considerably indebted to a number of monographs and review articles. Among these should be mentioned specially L. Pauling's important work *The Nature of the Chemical Bond* which, together with Pauling's other publications, has largely governed the treatment of the covalent bond in the first chapter, also A. Farkas's *Light and Heavy Hydrogen*, G. v. Hevesy's *Das Element Hafnium*, I. and W. Noddack's monograph *Das Rhenium*, and G. T. Seaborg's review of artificial radioactivity in the *Chemical Reviews* for 1940.

My thanks for valuable criticism and suggestions are due to a number of friends and colleagues, above all to Dr. H. D. Springall and Dr. D. D. Eley, who have been good enough to read parts of the manuscript or proofs. It is too much to hope that a volume covering so many widely different and, in many cases, recently developed aspects of the science will be entirely free from errors and omissions;

but it is nevertheless hoped that the book will be of use as a convenient résumé of the enlarged scope of modern inorganic chemistry.

I should also like to express my appreciation to the staff of the Clarendon Press for their consistent helpfulness, and for the very high degree of technical skill and knowledge which has greatly facilitated the smooth setting up of the book.

E. B. M.

BRISTOL,
March, 1947

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I

PHYSICAL INTRODUCTION

THE systematization of inorganic chemistry within the framework of the periodic system, which was the outstanding feature of its earlier development, has now been followed by a phase in which the scope of the science has been enlarged in a revolutionary manner by an increased knowledge of atomic structure and by the application of the newer theories of matter and energy.

In this way entirely new fields have been opened. Thus, while ordinary changes of temperature or of other physical conditions only affect molecular or, at the most, extranuclear atomic energy states, the recognition of the wide practicability of reaching down into the atomic nucleus by the equivalent methods of bombardment with particles or with sufficiently large radiation quanta has opened a new field of more deeply seated or nuclear chemistry in which nuclear levels are raised to a value sufficient to cause rupture and the production of new nuclei. This type of reaction, supplemented by methods for the separation of naturally occurring isotopes, has already enlarged the list of elementary atoms to an extent undreamed of in classical theory, in that each element has now become a generic term for a varying number of isotopes, some of which are stable and some radioactive. Since artificial radioactive isotopes can be made throughout the whole range of the periodic system, they have become of great importance in detecting exchange reactions and in following other processes in which the course of an individual atom has to be traced among other atoms of the same element. Further, since all isotopes of a given element possess substantially the same chemical properties, it has in special cases been possible to utilize artificially produced isotopes for the determination of the properties of a difficultly accessible element prior to its actual isolation from natural sources. An example of this is to be found in Element 85. Nuclear reactions have, moreover, given at least two artificial elements—Element 93 (neptunium) and Element 94 (plutonium)—which lie beyond uranium (Element 92) and consequently beyond the hitherto accepted limit of the periodic system. There is no precedent for placing these transuranic elements in their appropriate vertical groups and for predicting their electronic configurations and probable

properties from ordinary periodic considerations, all the more since a new horizontally related transition group of unstable elements, starting from uranium and comparable with the horizontally related rare earths, may exist. Plutonium has recently become of considerable importance as an alternative to ^{235}U for the release of atomic energy by nuclear fission.

Inorganic chemistry has necessarily also been greatly influenced by many of the other newer physical conceptions: thus the drawing up of energy-mass balances for nuclear reactions follows from the acceptance of the relativistic theory of the equivalence of energy and mass and of the reversible transformation of one form into the other. The theoretical side of the science has also been affected greatly by the wave aspect of matter and by the results of quantum-mechanical treatment, which have paved the way for an entirely new picture, firstly of the nature of particles, atoms, and molecules and, secondly, of the various types of directed and non-directed valency bonds by means of which atoms are linked together: indeed, it is only from this aspect that any theory of the nature of the covalent bond can be advanced.

Much has also been done to extend our knowledge of molecular size and shape, principally by the determination of interatomic distances (and consequently of valency angles) by X-ray or electron diffraction methods or by the interpretation of spectroscopic data. Molecular shape and interatomic distances are closely bound up with the nature of the bonds involved; and the conception of resonance between two or more possible electronic configurations for the same system, in such a way as to give a hybrid structure stabilized by resonance energy, has been used to explain the many known cases of exceptional molecular stability or abnormal bond lengths.

Side by side with these fundamental advances, chemistry has also expanded along more normal lines. The periodic system has now probably been completed by the isolation, or the artificial preparation, of all the possible elements up to uranium, the evidence being weakest for Elements 61 (a rare earth), 85 (eka-iodine), and 87 (eka-caesium). Further, a large number of new compounds of the commoner elements—such as the oxides of fluorine and of bromine—have been successfully prepared.

Before beginning a summary of recent progress in some representative sections of inorganic chemistry, it appears desirable to give an

outline of some of the newer physical conceptions which underlie modern chemical theory. In this, emphasis will be laid on the results, in so far as they affect a better understanding of the structure and properties of the elements and of their inorganic compounds, rather than on the experimental technique involved in this physical approach.

MASS-ENERGY RELATIONSHIPS

The interconvertibility of matter and energy, which is one of the results of the special theory of relativity, follows the equation:

$$E = mc^2, \quad (i)$$

in which m is the mass, in grams, which is converted into energy or created out of energy. E is the corresponding energy, in ergs, and c is the velocity of light in cm. per sec.

According to this principle matter may be viewed as merely a special form of localized energy; and any change in the energy of a system may be regarded as a change in its mass.

On the basis of the above equation:

$$\begin{aligned} 1 \text{ gram mass is equivalent to: } & 8.99 \times 10^{20} \text{ ergs}^\dagger \text{ energy} \\ & = 5.61 \times 10^{32} \text{ electron volts energy} \end{aligned}$$

or:

$$\begin{aligned} 1 \text{ atomic mass unit is equivalent to: } & 1.49 \times 10^{-3} \text{ erg} \\ & = 9.31 \times 10^8 \text{ electron volts.} \end{aligned}$$

An electron volt, which is given as an alternative unit of energy, is the amount of energy acquired or lost by a particle of unit electronic charge on passing through a potential difference of one volt. It is a very small unit (1.602×10^{-12} erg); and the energy of atomic particles is often expressed in millions of electron volts (Mev.). One Mev. corresponds with 0.001074 atomic mass units on the physical scale.

The conversion of matter into energy provides an explanation of phenomena such as the annihilation of unstable mass particles and the small but measurable losses in mass observed in interactions between high-energy particles and atomic nuclei. Moreover, since the conversion is reversible, it follows that matter can actually be created out of energy. An example of this will be given later in connexion with Fermi's explanation of the mechanism of the creation of electron-positron pairs.

[†] Strictly, mass and energy cannot be equated by an ordinary = sign since they possess different dimensions.

Energy resulting from the conversion of matter is, in general, evolved as short-wave radiation (γ -rays), although part may remain in the system as binding energy and contribute to its stability. Accordingly, the mass defect of a compound particle, compared with the sum of the masses of its components, is found to give an indication of the stability of the bonds by virtue of which the compound particle is held together. For example, the mass of a deuteron, which is made up of a neutron and a proton, is approximately 0.002 atomic mass units less than the mass-sum of the constituent proton and neutron, corresponding with a binding energy of about 2 Mev. if all the energy is used in the link. This relatively low binding energy, compared with about 28 Mev. for the α -particle, explains why the deuteron can be disintegrated, with rupture of its bond, and why the α -particle has so far resisted disintegration.

Relativistic Increase of Mass with Velocity

Since the kinetic energy of a particle increases with its velocity, it would be expected—if only on grounds of energy-mass conversion—that its mass would also increase. The precise formulation of this increase follows from the theory of relativity and is given by the relationship:

$$\frac{m_v}{m_0} = \frac{1}{\sqrt{1-v^2/c^2}}, \quad (\text{ii})$$

in which m_v is the effective mass at the velocity v , and m_0 is the rest mass, i.e. the mass of the particle at rest. This relativistic increase of mass with velocity only begins to be appreciable at velocities approaching that of light. It has, however, actually been observed, for instance in the case of fast-moving electrons. One result of the above equation is that particle speeds equal to or above that of light are impossible, since the mass would become infinite.

ULTIMATE PARTICLES

From the classical standpoint the smallest particle was the atom. This conception of matter had to be abandoned on the discovery of the electron and, later, of other small mass entities which seem to constitute natural units of matter of an order below that of the atom or molecule. Some of these so-called ultimate particles are capable of stable existence both in the free state and apparently also within the atom (from which they can be expelled by sufficiently energetic treatment): others have only short lives and, while they come into

being for short times as free material particles resulting from the materialization of energy, their existence within the atom, if they are found there at all, can only be a transient one. An example of this will be discussed later in connexion with the emission of positrons by artificial radioactive elements.

Stable Particles

Three stable ultimate particles are known: the electron, the proton, and the neutron. Of these, the electron has been known for too long to warrant a detailed description in this introduction; and it will be sufficient to note that (in addition to their emission during radioactive changes) electrons can be produced in a free state by even a superficial decomposition of all the elements, whereas the expulsion of protons is a far more deeply seated effect which, save in the special case of hydrogen, can only be brought about by the absorption by the decomposing atom of far larger energy quanta as a result of exposure to high-energy radiation or, more usually, by reason of large energy-changes resulting from particulate bombardment. Many examples of the production of protons by both methods will be given in connexion with various nuclear reactions. A proton, from whatever source it is produced, is found to be identical in every respect with a hydrogen atom from which an electron has been removed. Its mass is consequently approximately unity on the atomic scale, the corresponding mass of an electron being only 0.00055. The proton possesses an inherent positive charge equal in magnitude to the negative charge of the electron (4.803×10^{-10} e.s.u.).

The discovery of the neutron is relatively recent. Unlike the proton or the electron, it cannot, on account of its electrically neutral nature, be detected by means of a cloud chamber or ionization chamber, nor is it deflected in a magnetic field; and evidence for the presence of free neutrons has usually to be inferred from collision effects, i.e. from the ionizing particles or high-energy radiation which these moving neutral particles produce by collision with atomic nuclei. The recognition of the particulate nature of the neutron is, in the first instance, due to Chadwick,[†] who showed that the supposed high-energy γ -rays observed by Bothe and Becker[‡] as a product of the bombardment of beryllium with α -particles cannot, on energetic

[†] J. Chadwick, *Proc. Roy. Soc.* 1932, A 136, 692

[‡] W. Bothe and H. Becker, *Z. Physik*, 1930, 66, 289

grounds, correspond to radiation quanta and are in reality electrically neutral particles of approximately unit mass.

It should be noted that evidence for the occurrence of neutrons as universal constituents of all the elements (except hydrogen) has been obtained by bombarding these with high-speed particles or with γ -radiation. Heavy elements are more resistant to the expulsion of their neutrons than lighter elements; but ejection of the neutrons from heavier atoms is probably only dependent on the availability in practice of bombarding particles or radiation of sufficiently high energy.

As a practical source of neutrons a mixture of a radium salt with a beryllium salt has been widely used. Neutrons are also produced in relatively high yield and with a high degree of freedom from accompanying radiation by the action of deuterons on deuterium. Other methods include the action of deuterons on lithium, or of γ -radiation on deuterium, which gives neutrons of a single known energy.

Composite Particles

Although any atom or ion may be regarded as a composite particle, two compound particles, in particular, have been widely used as projectiles. The longest known of these is the α -particle, which is ejected during the spontaneous decay of heavy radioactive elements and is a frequent product of nuclear reactions generally. This particle has a mass of about 4 on the atomic scale and a two-unit positive charge. It is identical with a helium nucleus and it is thus an association of two protons and two neutrons; but it is sufficiently resistant to decomposition for its disintegration never to have been observed, and it probably exists as such in the nuclei of many elements.

Another extensively used composite particle, the deuteron, bears the same relation to deuterium as that of the proton to hydrogen. It is composed of one proton and one neutron; and, since it is a deuterium atom less an electron, it has a mass of approximately 2 and a unit positive charge. This association is, as already stated, far less stable than the two-proton two-neutron complex which constitutes the α -particle; and it has been successfully disintegrated, for instance by high-energy γ -rays.

It will be seen from a later chapter that deuterons form very effective projectiles for atomic disintegration and, especially when

accelerated to high velocities by means of a cyclotron or similar device, readily penetrate to the nucleus of a target atom.

Unstable Particles

While the ordinary or negative electron is capable of indefinitely long existence, its positive counterpart, the so-called positron—which was first detected in cosmic radiation†—is unstable. The positrons in this radiation are usually formed, apparently by the materialization of energy, in the form of positron-electron pairs (although cases of the apparent occurrence of positrons alone also exist); and they undergo subsequent annihilation, with reproduction of energy, by collision with an electron, the electron being also annihilated.

In addition to their occurrence in cosmic rays, positrons are a frequently occurring product of the decay of artificial radioactive elements; and they may be produced by the action of high-speed particles or high-energy radiation (e.g. γ -radiation from thorium-C) on matter.‡ The mass of the positron is approximately equal to that of the negative electron; and its charge (positive) is equal in magnitude to the electronic charge.§

The existence of two further ultimate particles, also of small mass but of zero charge, the neutrino and the anti-neutrino, has been postulated to explain the energy continuum (see p. 19) observed in certain radioactive changes (β -ray disintegration), the hypothetical neutrino being associated with, and sharing the energy of, the electrons, while the anti-neutrino occupies a similar position with regard to the positrons. The detection and even the certain recognition of the existence of these very small electrically neutral particles is exceedingly difficult, if only for the reasons mentioned in connexion with the much more massive and well-established neutron; and the relationship between an electron and a neutrino, or between a positron and an anti-neutrino, is obscure and of a different character from that between a proton and a neutron. All these unstable particles are of less interest from the standpoint of the normal structure of the atom than the three stable particles (the neutron, proton,

† C. D. Anderson, *Science*, 1932, **76**, 238; *Phys. Rev.* 1933 (ii), **43**, 491; P. M. S. Blackett and G. P. S. Occhialini, *Proc. Roy. Soc.* 1933, A **139**, 699.

‡ C. D. Anderson, *Science*, 1933, **77**, 432; I. Curie and F. Joliot, *Compt. rend.* 1933, **196**, 1581; L. Meitner and K. Phillip, *Naturwiss.* 1933, **21**, 468.

§ See, for instance, the direct measurements of A. H. Spees and C. T. Zahn, *Phys. Rev.* 1940 (ii), **58**, 861.

and electron), since any units of the unstable series can, at the best, only possess a very short individual existence within the atom, if they are formed at all in nuclei other than radioactive ones.

Finally, the possibility of the existence of an unstable particle intermediate in size between the unit-mass (proton-neutron) series and the small series has been predicted on theoretical grounds by Yukawa.[†] This intermediate particle, the mesotron, seems to be produced out of cosmic radiation. Its rest mass appears to lie between 150 and 250 times that of the electron: thus, recent measurements[‡] have given a value of 240 ± 20 times the electronic mass, but mesotrons of differing masses may possibly exist. The mesotron carries a single electronic charge and undergoes spontaneous radioactive decay with production, *inter alia*, of electrons.[§] The calculated mean life is of the order of 10^{-6} sec.; and, from its tracks in a cloud chamber, both positively and negatively charged mesotrons exist.

WAVE ASPECT OF MOVING PARTICLES

An essential property of matter is the possession of inertia, manifested, if the matter is in motion, by momentum, which is the product of the mass of the material particle and its velocity.

De Broglie and others have, however, shown that, in addition to their inherent momenta, small moving particles also show the characteristics (wave-length, etc.) of wave systems. Thus, if a stream of electrons is allowed to impinge on a diffraction grating of suitable spacing (e.g. on a crystal lattice) diffraction effects are observed of a nature similar to those which would be given by a wave train of wave-length corresponding with de Broglie's equation:

$$\lambda = \frac{h}{\text{momentum of particle}} = \frac{h}{mv}, \quad (\text{iii})$$

in which h is Planck's constant (6.624×10^{-27} erg-sec.) and m and v are the mass and velocity of the particle. If m and v are expressed in grams and in cm. per sec., the equivalent wave-length is obtained in centimetres. The close analogy of moving electrons to radiation quanta is further shown by the possibility of constructing electron microscopes, in which the electrons are focused by a magnetic field

[†] *Proc. Phys. Math. Soc. Japan*, 1935, **17**, 48; 1938, **19**, 712.

[‡] L. Leprince-Ringuet, S. Gorodetzky, and R. Richard-Foy, *Phys. Rev.* 1941 (ii), **59**, 460.

[§] E. J. Williams and G. E. Roberts, *Nature*, 1940, **145**, 102, 151; E. J. Williams and G. R. Evans, *ibid.* 818.

in a similar fashion to light rays refracted by a lens, but giving an enormously increased resolving power. The photographs thus obtainable of submicroscopic bacteria and other objects too small to be sharply defined if ordinary light is used are a striking experimental demonstration of this wave aspect of the electron.

Diffraction effects are also given by larger particles, such as protons or α -particles; but the observation of the wave character of these larger particles becomes more difficult by reason of the operation of Heisenberg's uncertainty principle (see p. 12).

Observations of the above type have led to the general wave theory of matter, according to which material particles, and indeed all matter, are to be regarded merely as localized wave systems of some sort. The wave packet constituting a particle is usually viewed as a concentration—in the form of a standing wave system—of existing free waves, the free wave motion from which the wave packet is built up being apparently continuous in existence and universally distributed throughout space. Nothing is known of the medium in which the vibrations corresponding with these particle-waves occur, save that this medium cannot be the so-called ether, which had to be postulated as the 'something' carrying the electromagnetic waves involved in radiation but about which, in turn, although it has become a familiarized conception, only negative knowledge is available. It must be emphasized that although particles, from this wave aspect, somewhat resemble radiation quanta, and although free radiation quanta can be shown to possess some of the essential properties of mass particles, the analogy cannot be pushed too far, if only from the fact that the propagation of free radiation is tied to an almost constant high rate, whereas the velocity of a particle can have any value below the order of the speed of light.

If a particle consists of, or is accompanied by, a wave concentrate or wave packet, two methods of wave concentration seem possible. In the first place, as has been pointed out by Heisenberg,[†] if space is regarded as containing a large number of wave trains travelling at slightly differing velocities and having slightly differing wave-lengths, then the combination of suitable trains may lead to a cancellation of the vibrations of these trains except over a small region of space in which they add up to form a wave packet which moves forward

[†] See S. Tolansky, *Introduction to Atomic Physics*, Longmans, Green & Co., 1942, p. 193.

with a velocity of its own, this velocity being different from the general speed of propagation of the wave. The velocity of this wave packet is known as the group velocity. The speed of the component waves (postulated as not differing greatly from one component to another) is called the phase velocity.

It is, further, of great interest to remember that, if waves of the *same* velocity but of slightly differing wave-lengths are compounded, this superposition will lead to concentrates (beats) which will travel at the same velocity as the general speed of the component waves. This type of combination is reminiscent of free radiation quanta and might form a link between such quanta and material particles if the vibrating media were not in all probability different.

A wave packet might alternatively be visualized as a system of standing waves, localized by some form of reflection or constraint. Its treatment from this aspect, rather than as purely an amplitude concentration of free waves, involves less simple considerations as to the method of its reflection, although the necessity—inherent in the free-wave superposition theory—for the regular recurrence of particles is avoided.

It will be noted that the de Broglie waves corresponding with or accompanying a moving particle have a wave-length determined by the velocity of the particle relative to the grating, namely by the group velocity of the wave packet; and there seems to be no reason why these particle waves—the reality of which can be tested experimentally—should not (unlike some of the probably subjective waves of wave mechanics) be regarded as objective realities corresponding with actual physical vibrations in ordinary three-dimensional space.

The following evidence is commonly put forward to show that particle waves cannot be waves in the ordinary ether on grounds that the phase velocity in the wave packet is greater than that of light.

Let v_p be the phase velocity of the wave within the wave packet, and let ν and λ be the corresponding frequency and wave-length. Then, since $\nu = v_p/\lambda$, Planck's quantum relationship, $E = h\nu$, becomes $E = hv_p/\lambda$; or, introducing the mass-energy equation already given:

$$mc^2 = E = \frac{hv_p}{\lambda}. \quad (\text{iv})$$

If v is the group velocity of the wave packet as a whole, namely the ordinary velocity of the particle (on which, as already stated, the

de Broglie equation is based), then, on substituting h/mv (equation iii) for λ in (iv), this simplifies to:

$$vv_p = c^2. \quad (v)$$

Hence, since the ordinary velocity, v , of the particle must, by virtue of the relativistic increase of mass with velocity, always be less than c , the phase velocity, v_p , must be greater than c .

One difficulty connected with the wave-packet theory has been to find an explanation for the permanence—or at any rate the long life—of the wave packet, since ordinary wave concentrates are short-lived only and are quickly dissipated. To do this it has been necessary to introduce the conception of a localizing or guiding wave (Schrödinger's wave function), which controls the significant extension of the wave packet in space and leads to a derived function (the probability distribution function) which gives the particle-wave density within the packet, i.e. the probability of the occurrence of the particle at a given point in the packet.

Particulate Aspect of Radiation

This aspect, which was foreshadowed in Newton's corpuscular theory and which was taken a step further by Planck's conception of discrete energy packets or quanta, has become a necessary consequence of experimental evidence that photons, in addition to their wave characteristics, also possess momentum.

This is shown, for instance, in the Compton effect, in which collisions between photons and the electrons of an atomic structure are found to obey the momentum laws like collisions between material particles. As a result of such collisions part of the energy of the photon is transmitted to the electron with which it collides; and the loss of this energy in the rebounding photon is manifested, from its wave aspect, by a decrease in its frequency, energy and frequency being connected by the relationship: $E = h\nu$. Further, as will be seen from many examples given later, high-energy (i.e. high-mass) photons, such as occur in γ -rays, constitute projectiles which are as effective as high-energy mass particles in causing nuclear reactions: indeed, bombardment with such photons is widely used as an alternative and completely equivalent method to particulate bombardment.

Reference has already been made to difficulties in regarding the 'mass' of a photon as being completely identical with that of a

material particle. With this reservation the equivalent mass of a photon follows from the identity:

$$h\nu = E = mc^2,$$

from which the mass is $h\nu/c^2$ and the momentum (mc) is $h\nu/c$. It may also be noted that, for photons, which move at the speed of light, the equivalent of de Broglie's equation for the wave-length of a mass particle can be obtained directly by inserting wave-lengths (from the relationship: $c = \lambda\nu$) in place of frequencies in the above equation. Expressed in this way, $h\nu = mc^2$ becomes:

$$\lambda = \frac{h}{mc}.$$

The mass of some typical radiation quanta is given in Table 1.

TABLE 1

Nature of radiation	Approximate frequency	E , in ergs, of energy quantum	Mass of quantum	
			(a) in grams	(b) in terms of the mass of an electron
Short γ -rays .	10^{20}	0.7×10^{-6}	0.7×10^{-27}	0.8
Hardest X-rays .	10^{17}	0.7×10^{-9}	0.7×10^{-30}	0.0008
Yellow light (sodium D-line) .	5×10^{14}	3×10^{-12}	3×10^{-33}	3×10^{-6}

It will be seen that the shortest γ -rays, as emitted from radioactive substances, occur in quanta having a mass of the order of that of an electron (0.9×10^{-27} gram).

Wave and Particle Aspects and the Uncertainty Principle

According to Heisenberg's uncertainty principle† two dynamical quantities appertaining to a system can be accurately measured at the same time only if these quantities are of such a nature that a special condition (the vanishing of their commutator in the branch of algebra known as matrix mechanics) is satisfied: otherwise any trend of physical conditions which is conducive to an increasingly accurate measurement of one quantity will lead to an increasing uncertainty in the measurement of the other. The properties which

† W. Heisenberg, *Z. Physik*, 1927, **43**, 172; *The Physical Principles of the Quantum Theory*, University of Chicago Press, 1930; L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Publishing Co., 1935, p. 428.

a particle-wave possesses, on the one hand as a particle and on the other as a wave system, fall within the latter category.

If the de Broglie equation is written in the form:

$$\text{momentum} \times \lambda = h,$$

in which the momentum is the particle characteristic and λ the wave characteristic, it will be seen that a long wave-length corresponds with a small value for the momentum and vice versa. Since a relatively long wave-length can be measured with a greater fractional accuracy than a short length, it follows that, for the accurate evaluation of this wave property, the particle property (momentum) must be small. On the other hand, the possession of a large momentum will be conducive to an accurate determination of this particle characteristic, but will involve a small value of λ and consequently lead to a relatively inaccurate determination of this wave property. These considerations apply both to ordinary material particles and to photons. The wave properties of matter are accordingly most easily and accurately observed with the lightest of all particles, namely with electrons, whereas the mass aspect of radiation quanta becomes most pronounced with photons of short wave-length (γ -rays). The equivalent wave-length of an electron can of course be still further increased by decreasing the speed; and it has in this way been possible to produce electron-diffraction effects by means of an ordinary ruled grating, although the reduction in speed cannot be pushed too far on account of practical difficulties in observing the effect.

Many other conjugate physical properties are connected by the uncertainty principle in a similar way; but the fundamental and general character of the principle is perhaps best seen by the impossibility of measuring both time *and* space† with equal certainty under the same observational conditions.

STRUCTURE OF THE ATOM

General

In order to obtain a clear picture of the structure, especially of a complicated atom, it is necessary to consider this from a particle rather than from a wave aspect, although conceptions such as definite electronic orbits may also be viewed as maximum-density

† See Sir James Jeans, *The New Background of Science*, Cambridge University Press, 1933, p. 232.

(i.e. maximum-probability) regions defined by a wave-mechanical function. According to the Rutherford-Bohr atomic model, an atom consists of a positively charged nucleus, which is relatively small† in comparison with the size of the whole atom and in which the mass of the atom is almost entirely concentrated, this nucleus being surrounded by a planetary system of electrons, the motion of which is confined to definite orbits; but, even from the particle aspect, the conception of actual orbits is unnecessary, save for visual clearness, since the planetary electrons may be regarded merely as existing in different quantized energy states in place of being confined to planetary orbits. On excitation these electrons pass from a normal orbit or energy level to a higher orbit or level, the step—or the reverse change involved in falling from an excited level to a lower atomic state—being accompanied by the absorption or emission, respectively, of radiation of frequency given by the relationship: $E_2 - E_1 = h\nu$.

Constitution of the Nucleus

On the basis of disintegration evidence, the nuclei of the various chemical elements appear to consist of an aggregate of protons and neutrons, the number of which increases progressively with the atomic mass of the element. Since each of the ultimate particles involved has a mass of approximately unity, the nuclear mass of a given element, on the atomic scale, should, if mass were strictly additive, be equal to the total number of protons plus neutrons contained in it: this number is known as the mass number, A , of the element. The chemical properties of the element will be determined, on the other hand, not by the mass number but by the number of protons alone (the atomic number, Z), since this—in that it represents the nuclear charge—in turn determines the number of extranuclear electrons and hence the extranuclear structure, which is responsible for the greater part of the chemical character of the atom. Atoms having identical atomic numbers but differing in their mass numbers are called isotopes of the same element.

From a numerical standpoint, the gradual building up of the nucleus, as the atomic number scale is ascended, is simple. Thus, the nuclei of the three hydrogen isotopes—ordinary hydrogen, deuterium, and the artificial radioactive hydrogen of mass 3—all contain one proton, corresponding with the unit atomic number of hydrogen,

† Atomic nuclei have diameters of the order of 10^{-12} cm. The effective diameter of an atom is of the order of 10^{-8} cm.

and consequently all have to a high degree the chemical properties of ordinary hydrogen; but they differ in containing, respectively, zero, one, and two neutrons, corresponding with nuclear masses of one, two, and three. It is usual to denote the atomic number and nuclear mass number by means of a subscript and superscript, placed most commonly on the left-hand side of the usual atomic symbol, the subscript denoting the atomic number (or nuclear charge) and the superscript the mass number: the above three isotopic modifications of hydrogen† are accordingly written: ${}^1_1\text{H}$, ${}^2_1\text{H}$, and ${}^3_1\text{H}$. Similarly, the nucleus of the next higher element, helium ($Z = 2$), contains two protons and, since it has an atomic mass of 4, two neutrons in addition. The two isotopes of the next element, lithium ($Z = 3$), will thus contain three protons, ${}^7\text{Li}$ (the more abundant form) having four neutrons, and ${}^6\text{Li}$ three neutrons, in addition to the protons, and so throughout the atomic series up to uranium ($Z = 92$), the nucleus of which contains 92 protons and sufficient neutrons to bring the nuclear mass to 238 in the case of the commoner isotope, ${}^{238}\text{U}$, or to 235 for ${}^{235}\text{U}$.

Little is known with regard to the arrangement of these protons and neutrons within the nucleus, although views have been expressed‡ on the presence of proton and neutron shells, the structure of which varies periodically in a somewhat similar manner to the extranuclear electronic structure; and there is, in addition, some probability of the inclusion of two-proton-two-neutron complexes corresponding with pre-formed α -particles, the evidence for this being the frequent expulsion of α -particles as a result of nuclear disintegration.

Stable and Unstable Nuclei

Nuclei may be stable or may disintegrate spontaneously, with emission of particles (electrons (β -particles), positrons, and α -particles) and radiation (γ -rays). It should be noted that protons and neutrons, which are a common product of artificial disintegration by bombardment, are not evolved during spontaneous decay.

Since the arrangement of the particles (protons and neutrons) within the nucleus is unknown, the nuclear conditions leading respectively to stability or instability cannot at the present time be stated

† As an exception, ${}^2\text{H}$ is usually written D (or ${}^2\text{D}$).

‡ See, for instance, H. A. Bethe and R. F. Bacher, *Rev. Mod. Phys.* 1936, 8, 82.

with any precision; and it is only possible to point out some general regularities. It has long been recognized that all very heavy elements are radioactive. Thus all elements of atomic number exceeding 83 have few or no stable isotopes. These elements are polonium (84), eka-iodine (85), radon (86), eka-caesium (87), radium (88), actinium (89), thorium (90), protactinium (91), and uranium (92); but, in addition to these heavy elements, radioactivity is also exhibited by naturally occurring isotopes of lighter elements ($^{40}_{19}\text{K}$, $^{87}_{37}\text{Rb}$, $^{148}_{62}\text{Sm}$, and $^{176}_{71}\text{Lu}$); and, above all, the preparation of artificial radioactive isotopes of substantially all the elements has shown that factors other than a high atomic number can induce instability.

Stability and the Neutron-Proton Ratio

Highly suggestive results are obtained from a study of the influence of the ratio of neutrons to protons in the nuclei. For instance, if this neutron-proton ratio, r , of all the elements, both stable and radioactive, is plotted against the atomic number, interesting regularities become evident. Some of these are shown in Fig. 1, which contains this plot for elements of atomic numbers 1 to 36, covering the first three horizontal rows of the periodic system. Stable isotopes are shown as black circles. The nature of artificial radioactive isotopes is indicated by the insertion in the open circles of a + or a - sign to denote, respectively, emitters of positive or negative β -particles (positrons or nuclear electrons) and by the insertion of a \times sign for cases in which stabilization occurs by K -electron capture, which is closely related to positron emission. For details of these processes, reference should be made to Chapter VII. In a number of cases, including ^{49}Ca , ^{44}Sc , ^{60}Co , ^{69}Zn , ^{80}Br , and ^{87}Kr in the range shown in the figure, two radio-isomers of an otherwise identical isotope exist (see p. 232); and the radioactive isotope ^{83}Kr is isomeric with a stable isotope of krypton of the same mass number. Radioactive ^{40}K occurs naturally.

On reference to Fig. 1 it will be seen, in the first place, that the position of radioactive hydrogen, ^3H , is symmetrical with that of ordinary hydrogen, ^1H , above and below the ratio-equality line ($r = 1$), on which deuterium, ^2H , stands. Secondly, stretching over the first two periods (and extending partly into the third), two regular series of isotopes of odd mass number (Curves I and III) occur, again symmetrically disposed as mirror images about the ratio-equality

line, but respectively stable ($r > 1$) and unstable ($r < 1$) up to $Z = 20$, from which point the lower series ceases while the higher series becomes unstable. The ratio-equality line itself is occupied

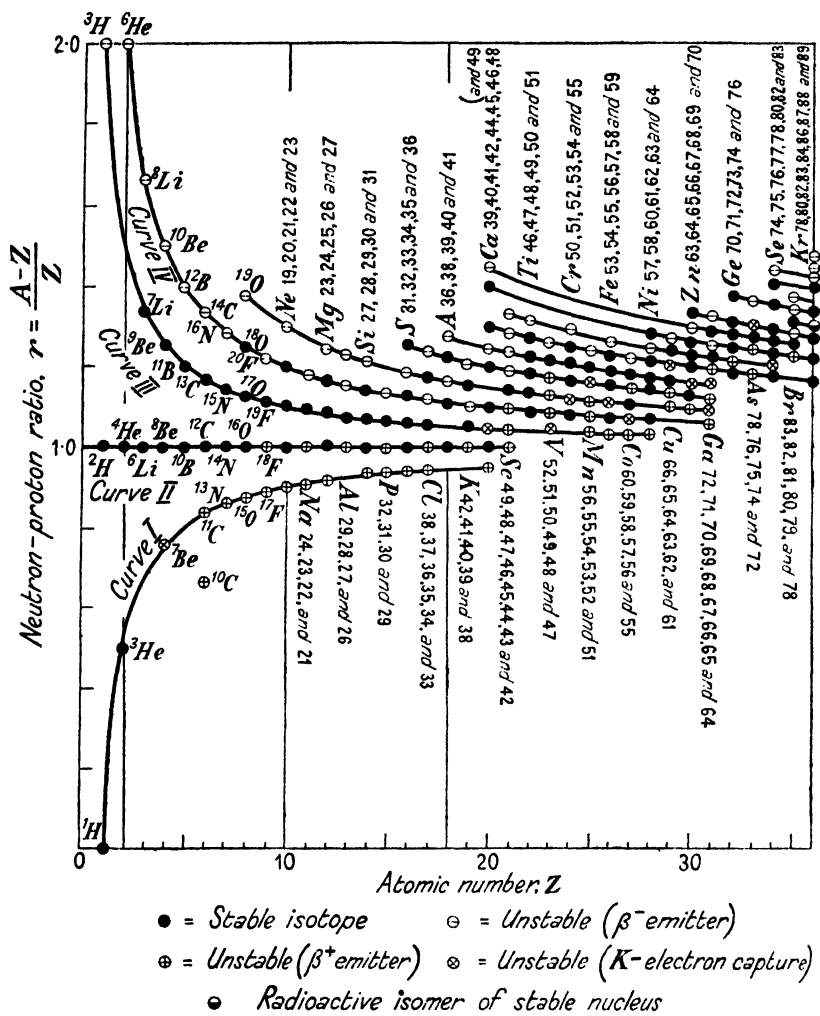


FIG. 1.

first of all (Curve II) entirely by stable isotopes of even mass numbers, including the artificial but stable beryllium isotope ^8Be , which does not occur naturally; but after $Z = 8$ this continuous stability changes to an alternation of unstable and stable elements; and

this alternate arrangement seems to be typical of all further series of even A (see Curve IV, after $Z = 7$, also Curves VI, VIII, X, and XII). As Z increases there is a general rise in the range of values of r corresponding with known isotopes until—as would be seen from a complete plot—no stable isotopes occur at high values of Z and r .

It will be noticed, further, that the type of radioactivity is regular: thus all isotopes in Curve I and all the unstable members of Curves II and III are positron emitters, with the exception of two elements (^{41}Ca and ^{47}V) in which K -electron capture occurs. Moreover, for any given element, namely, for any given value of Z , the electron-emitting isotopes usually have a higher neutron-proton ratio than the positron-emitting isotopes, i.e. the possession of an increased proton content seems to lead to an increased probability of the emission of positive electrons, whereas the possession of a smaller proton content is apparently conducive to the emission of negative electrons. Finally, the properties (stability or instability and, if unstable, the nature of the particles emitted) of isotopes not yet prepared can obviously in many cases be predicted from the position of the missing isotope in the curves.

All the above regularities, and especially the regular appearance of fresh curves as Z is progressively increased, suggest some sort of regular arrangement, possibly periodic, in the intranuclear protons and neutrons. With regard to pre-formed α -particles, it should be noted that spontaneous emission of these only occurs, as far as is known, with ^8Li and with very heavy elements, although they may be obtained from many elements by bombardment.

Nuclear Energy Levels

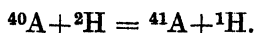
There is considerable evidence that an atomic nucleus is capable of existing in different quantized energy states. Thus, transitions between nuclear energy levels are apparently responsible for the observed occurrence of definite ranges of discrete energy quanta accompanying both the particles and the radiation (γ -rays) emitted from radioactive nuclei, just as transitions between extranuclear electronic levels are responsible for ordinary atomic spectra. The above energy steps are marked by the subdivision of the γ -ray photons into groups differing in frequency and, in the case of particles, into groups differing in range. The particulate energy differences are clear only for α -particle emission from a nucleus, since much of the

electron (β -particle) emission, especially from heavy radioactive elements, is due to the ejection of electrons from the extranuclear structure by the impact of γ -ray photons which, after emission from the nucleus, pass through this extranuclear structure: indeed the β -particle spectrum is closely connected with—and may be used as a measure of—energy differences in the γ -rays. A further complication in β -particle emission lies in the continuous background arising from the energy continuum which is observed for electrons or positrons having their origin in the nucleus (see next section) and already referred to in connexion with the postulation of the neutrino and of the anti-neutrino.

Other evidence for nuclear energy levels, particularly in artificial radioactive elements, occurs in connexion with the existence of isotopes of identical mass but of differing radioactive properties, this type of isomerism being probably based on intranuclear differences in rotational energy levels involving 'forbidden' transitions from the one level to the other. An example of this is given by the two forms of $^{80}_{35}\text{Br}$, having a half-life of 18 minutes and 4.4 hours respectively.

The presence of nuclear energy levels in stable as well as in unstable elements is also indicated by the resonance effects which facilitate the capture, during bombardment, of protons or slow neutrons of special energies, since, as has been pointed out by Bohr,[†] the probability of the formation of a new compound nucleus by projectile capture would be expected (especially if the various particles are viewed from their wave aspect) to be particularly high when the energy of the system, including the bombarding particle, is nearly equal to one of the energy levels of the compound nucleus.

Information as to the possible energy levels to which a nucleus may be raised on excitation can in many cases be obtained from the group energies of particles emitted in nuclear reactions other than spontaneous radioactive processes. A considerable amount of work has been done on this subject in recent years. As an example, Davidson[‡] found that on bombarding argon with 2.38 Mev. deuterons three proton groups of ranges 27, 35.75, and 53 cm. in air (corresponding with energies of 2.23, 3.01, and 4.37 Mev.) are emitted in the course of the reaction, which is probably:



[†] N. Bohr, *Nature*, 1936, **137**, 344; H. J. Braddick, *Ann. Reports Chem. Soc.* 1937, **34**, 9.

[‡] W. L. Davidson, *Phys. Rev.* 1940, **57**, 244.

These values for the group energies of the protons indicate excited states in the ^{41}A nucleus at 1.36 and 2.14 Mev.

Relationships between the Nuclear Particles

It may be noted that, while it is convenient to consider the nucleus as consisting of protons and neutrons only, other particles (e.g. electrons or positrons or electron-positron pairs) may be formed by the materialization of energy within the nucleus. Thus, Fermi† regards protons and neutrons as different inner quantum states of a single particle. Where a quantum jump between these states occurs, for instance spontaneously in radioactive elements or as a sequel to bombardment in the case of normally stable nuclei, this jump is considered to result in the creation, from energy, of an electron or a positron according as the initial state of the particle was the neutron or the proton state. The simultaneous creation either of a neutrino or of an anti-neutrino is also postulated, the pair of particles—i.e. electron and neutrino, or positron and anti-neutrino—being ejected from the nucleus, sharing between them the available energy. The ejection of electrons or positrons from a nucleus during radioactive decay may thus be no indication that the nucleus in question normally contains electrons in addition to larger particles: similarly, the stabilization of an unstable nucleus by capturing an extranuclear electron (*K*-electron capture) does not necessarily mean that this electron becomes a permanent member of the nucleus, since the phenomenon is only observed with positron-emitting nuclei and the captured electron may either undergo annihilation, by transformation into energy by reaction with a positron, or may pass into another material form.

Packing Fractions and Nuclear Binding Energies

While nothing is known either of the arrangement of the protons and neutrons within the nucleus or of the localization of intranuclear bonds, it is possible very simply to derive a gross figure for the total intranuclear binding energy which appears to be a dominating factor in determining the stability of a nucleus in the sense of its resistance to disintegration by bombardment. This total binding energy does not, however, enter so obviously into the property of spontaneous decay, which is probably due to the leakage of particles (as waves)

† *Z. Physik*, 1934, 88, 161; 89, 522; N. Feather, *Ann. Reports Chem. Soc.* 1934, 31, 395.

through a potential barrier, radioactivity being probably associated with special intranuclear configurations and certainly with the passage of the neutron-proton ratio across critical values.

The total intranuclear binding energy is the energy-equivalent of the mass which disappears, by transformation into energy, during the formation of a nucleus from its constituent particles. As the simplest example of this calculation of nuclear binding energy, the figures involved in the case of the deuteron,† to which reference has already been made, may be given. If the mass of a neutral deuterium atom, containing one neutron, one proton, and one extranuclear electron, is taken as 2.01471 on the physical scale ($^{16}\text{O} = 16$), the mass of its nucleus is this mass less the mass (0.00055) of the electron, namely, 2.01416. The most recent (1945) values for the masses of its constituent particles are 1.00893 for the neutron and 1.00758 for the proton, giving a total of 2.01651. The mass defect of the deuterium nucleus, compared with the mass-sum of its constituent particles, is thus $2.01651 - 2.01416$, namely, 0.00235 atomic mass units, or, expressed in energy units (since 1 milli-unit of mass = 0.932 Mev.), the binding energy is 2.2 Mev. The above values, particularly for the mass of the neutron and of the neutral deuterium atom, differ slightly from the somewhat older values used in a later section (see pp. 44–5); but the value for the calculated binding energy is not greatly affected by this.

In the special case of the deuteron, since only two ultimate particles are present, only one intranuclear bond can be involved, and this binding energy accordingly represents its strength. In more complicated nuclei only the number, A , of the constituent particles and not the number of intranuclear bonds or their variation in strength are known; but it is nevertheless possible, as has already been mentioned, to derive a figure in mass units for the average binding energy per individual particle by dividing the total mass defect of the nucleus by A , its mass number. Such figures are called packing fractions.

Since a nucleus of mass number A and atomic number Z contains Z protons and $(A - Z)$ neutrons, its packing fraction f_n , on the above basis, will be:

$$f_n = \frac{Zm_1 + (A - Z)m_0 - M_n}{A},$$

† H. A. Bethe, *Phys. Rev.* 1938, **53**, 313.

where M_n is the nuclear mass and m_1 and m_0 the masses of a proton and of a neutron.

Packing fractions based on the mass defect of the nucleus alone are not commonly used, particularly as it is possible, in many equations involving nuclear reactions caused by bombardment, to use the more convenient ordinary isotopic masses of the complete neutral atoms in place of the masses of the nuclei only, since the masses of the extranuclear electrons cancel out on both sides of the equation; and it has become conventional for the calculation of packing fractions to employ a system introduced by Aston, in which the packing of oxygen is taken as a standard (since oxygen forms the basis for atomic weights) and to express the mass-defect per particle for all other elements on a scale in which the packing fraction of oxygen is zero.

If I is the exact atomic weight of an isotope, Aston's packing fraction f is thus $(I-A)/A$, where A is the isotopic mass number; or, since A is always the nearest whole number to I ,

$$f = \frac{\text{the deviation of the at. wt. from the nearest whole number}}{\text{this whole number}}.$$

It should, for clearness, again be stated that the atomic masses used in this usual form of the packing fraction include the masses of the extranuclear electrons.

By virtue of the choice of oxygen as a standard, packing fractions expressed in this way may be positive or negative. Positive deviations of the isotopic weight from the whole number (i.e. excesses) lead to positive packing fractions and vice versa. Some of these deviations for a few of the isotopes of the lighter elements are given in Table 2, the values being due to Aston.†

TABLE 2

<i>Isotope</i>	<i>Isotopic weight</i> ($^{16}\text{O} = 16$)	<i>Packing fraction</i> $\times 10^4$
^1H	1.00812	+81.2
^2D	2.01471	+73.55
^4He	4.00391	+9.77
^{10}B	10.0161	+16.1
^{12}C	12.00355	+2.96
^{14}N	14.0073	+5.28
^{19}F	19.0045	+2.36
^{20}Ne	19.9986	-0.70

† F. W. Aston, *Proc. Roy. Soc.* 1937, A 163, 391.

The values of the packing fractions have also been determined by Bainbridge and Jordan,[†] by Mattauch and Herzog,[‡] and, for a large number of the heavier elements, by Dempster.[§] A curve of the form shown in Fig. 2 is obtained on plotting the packing

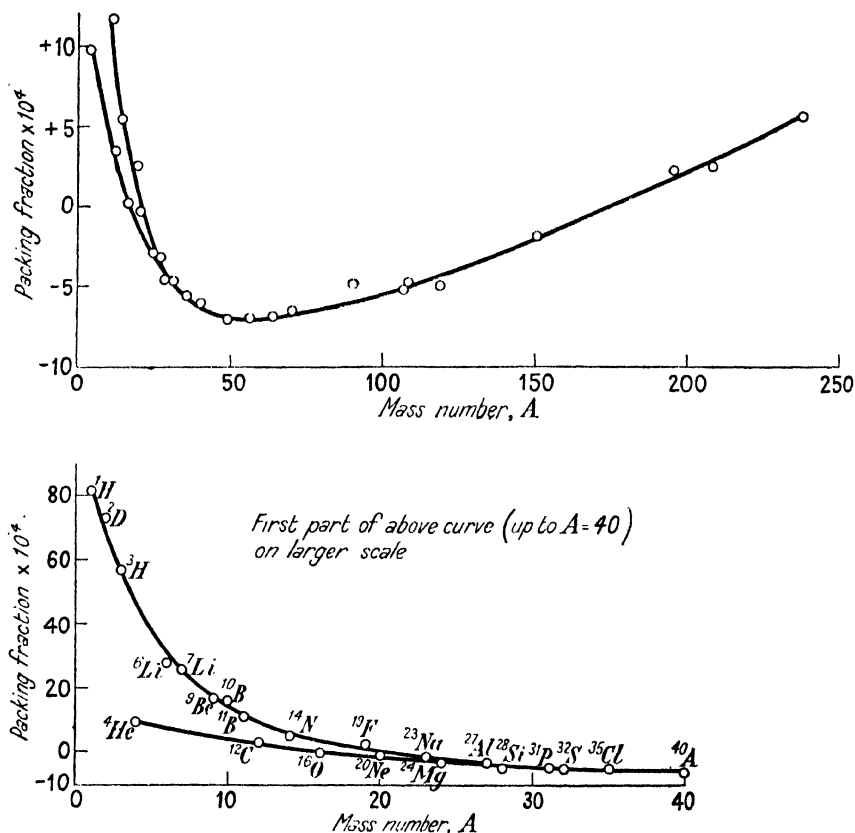


FIG. 2.

fractions against the mass numbers of the elements. This curve begins to correspond with negative values for the fraction at a mass number of 20 and passes through a minimum at about 50, rising gradually to positive values once more at a mass number of about 175. It will be seen that branching occurs with elements of low A if they are exact nuclear multiples of $\frac{1}{2}\text{He}$. For a critical discussion of

[†] K. T. Bainbridge and E. B. Jordan, *Phys. Rev.* 1937, **51**, 384, 385.

[‡] J. Mattauch and R. Herzog, *Naturwiss.* 1937, **25**, 747.

[§] A. J. Dempster, *Phys. Rev.* 1938, **53**, 64, 869.

differences in the exact values of the packing fractions, as determined by various investigators, reference should be made to reviews by Livingston and Bethe† and by Hahn.‡

From the results of Dempster, it is possible that Aston's values for the heavier elements may need adjustment; and in view of the fundamental importance of these packing fractions Dempster's values (marked with a (D)), have also been included in the list of isotopic weights contained in Table II of the Appendix.

Extranuclear Structure

The extranuclear electrons are, in the Rutherford-Bohr atom, regarded as moving in definite orbits round the nucleus, the number of these planetary electrons being, in a neutral atom, equal to the atomic number of the element, i.e. to the number of nuclear protons. Thus, the hydrogen atom ($Z = 1$) has one extranuclear electron only, whereas helium ($Z = 2$) has two; further, all isotopes of the same element, since they have the same atomic number, will have the same number—and the same arrangement—of extranuclear electrons. In place of considering the electrons as moving in actual orbits, they may be regarded merely as occupying definite energy levels.

An alternative, but less easily visualized, picture of electron distribution with respect to the nucleus can be obtained by the methods of wave mechanics.

The Bohr Atom

In view of the difficulty in visualizing the wave-mechanical atom, with its complicated change of shape as electrons occupy orbitals of different types, the extranuclear electronic configuration may be considered first of all from the standpoint of the Bohr model or, even more simply, on the basis of electronic energy levels alone. The Bohr model treatment of the atom is of historical interest and still provides a useful (and probably the clearest) physical picture of the constitution of an atom.

The arrangement of extranuclear orbits or energy levels and the occupation of these by electrons, in the normal or unexcited state, was shown, principally on spectroscopic evidence, to follow a relatively simple and regular pattern, in that—since any change of an electron from one possible orbit or level to another (for instance, from

† M. S. Livingston and H. A. Bethe, *Rev. Mod. Phys.* 1937, **9**, 245.

‡ O. Hahn, *Ber.* 1938, **71**, 1.

a normal to an excited level or vice versa) is governed by quantum laws and is thus accompanied by the adsorption or emission of radiation of frequency determined by the fundamental relationship $E_2 - E_1 = h\nu$ —information as to the number and heights of possible levels can be obtained from an analysis of the structure of atomic spectra.

This spectroscopic evidence has indicated the presence in the extra-nuclear structure, firstly, of a number of principal energy levels or orbits, usually denoted by the capital letters K, L, M , etc., or by the numbers 1, 2, 3,..., and, secondly, in each main level, of various sub-levels denoted conventionally by the small letters s, p, d, f , etc., or by the numbers 0, 1, 2, 3,... and representing minor energy variations in each of these main levels or secondary deviations from each of the main orbits. The numbers (or letters) denoting the main and subsidiary level or orbit occupied by an electron are known, respectively, as the principal and the secondary quantum numbers.

In addition to occupying a given sub-level, which in turn forms part of a principal level, an electron is characterized by the direction of its spin.† This possible rotational difference between electrons makes necessary the definition of the sense of the spin (positive or negative) by means of a spin number m_s , where $m_s \cdot h/2\pi$ is the component of angular momentum of the electron spin with respect to any prescribed axis.‡ This spin number can only have the values $+\frac{1}{2}$ or $-\frac{1}{2}$. All the above differences in the possible state of an electron can be deduced from an analysis of the fine structure of atomic spectra; but a still further subdivision in energy levels, which is not apparent from optical spectra alone, is indicated by the resolution of spectral lines into triplets by an external magnetic field (the so-called Zeeman effect).

Accordingly, in order to define the state of an electron four distinct quantum numbers are necessary, namely:

	Usual symbol	Possible numerical values (see below)
1. The principal quantum number, corresponding with the main order of the electron shell (K, L, M , etc.)	n	1, 2, 3,...
2. The subsidiary or azimuthal quantum number (s, p, d , etc.)	l	0,..., ($n-1$)
3. The spin quantum number	m_s	$\pm \frac{1}{2}$
4. The magnetic quantum number	m	$-l, ..., 0, ..., +l$

† G. E. Uhlenbach and S. Goudsmit, *Naturwiss.* 1925, **13**, 953.

‡ See, for instance, Pauling and Wilson's *Introduction to Quantum Mechanics*, Chapter VIII.

The possible values for the first, second, and fourth of these quantum numbers are connected by simple rules. In the first place, l , the subsidiary quantum number (which is also called the azimuthal quantum number since, in the elliptic theory of electron orbits, it represented the eccentricity of the elliptic orbit), can have any integral positive value from zero up to $n-1$, where n is the principal quantum number. Secondly, the magnetic quantum number m of an electron of subsidiary quantum number l can have any integral value (including 0) between $-l$ and $+l$. The maximum number of electrons in each main or subsidiary level is controlled by the Pauli exclusion principle, according to which no two electrons in the same atom can have all four quantum numbers in common.

From the above relationships between the various quantum numbers, it follows that in the first main orbit or level, K , for which $n = 1$, the only possible value of l (i.e. $n-1$), is 0; consequently m must in this case also have the single value zero; and this first main orbit can thus be occupied only by a single electron pair with opposed spins, or, of course, by a single electron.

In the second main level, L (for which $n = 2$), l may be 0 or 1, m may be -1 , 0, or $+1$, m_s being $\pm\frac{1}{2}$ as before. This gives eight possible different combinations of the four quantum numbers, the electrons being subdivided into two, with paired spins, in the zero or s sub-level ($l = 0$) and six—i.e. three sets of paired-spin electrons, each pair differing from the other pairs in the value of m —in the p sub-level ($l = 1$).

The maximum number of electrons in the various main shells and their distribution among sub-levels are summarized in Table 3. The

TABLE 3

Main shell or level	Total number of electrons	Distribution of electrons among subsidiary levels				
		s	p	d	f	...
K	2	2	—	—	—	
L	8	2	6	—	—	
M	18	2	6	10	—	
N	32	2	6	10	14	
O	(50)	2	6	10	(14)	...
P	(72)	2	6	(10)	(14)	...
Q	(98)	2	(6)	(10)	(14)	...

values for the electrons in the higher levels are enclosed in brackets in the table, since these levels are normally not occupied by electrons in the atomic series limited by uranium.

It is of interest, in connexion with the progressive building up of the electronic structure as the atomic number increases, to give the energy sequence for the various main and subsidiary levels. This is

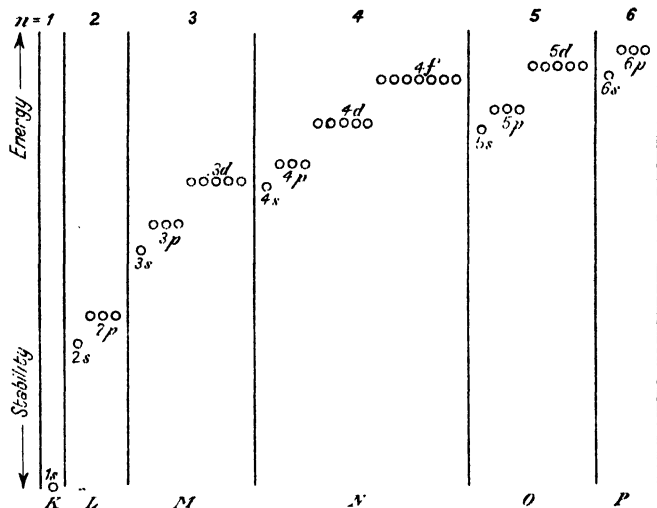


FIG. 3.

summarized diagrammatically in Fig. 3, which is based on values given by Pauling.[†] In general, an added electron falls into the lowest available level; but, as Pauling points out, if several sub-levels of approximately equal energy are available, the electrons added as the atomic number increases tend to occupy these levels singly before pairing occurs, i.e. the normal state of the atom will be that with the maximum resultant spin allowed by the Pauli principle: further, the shift or rearrangement of electrons between orbits of the same, or approximately the same, energy readily occurs.

The Wave-Mechanical Atom

It has been mentioned in an earlier section that, in the absence of a so-called guiding wave, the wave packets which represent electrons and other particles from their wave aspect would rapidly become dissipated. The theory of this localization of particle-waves, when

[†] *The Nature of the Chemical Bond*, Cornell University Press, 1940, p. 26.

applied to electrons lying in an atomic field, is of special chemical interest.

The mathematical laws followed in the localization of atomic electron-waves have been worked out largely by Schrödinger, who postulates, as the basis of these localization laws, a purely mathematical conception known (since it fluctuates both in time and along other coordinates in a manner similar to a wave) as a wave function Ψ . It is convenient to treat these non-time coordinates as if they corresponded with spatial variations in the governing function.

The variation of this function with time is, for a given electron, of the form

$$\Psi = \psi e^{2\pi i \nu t} = \psi e^{2\pi i (E/h)t},$$

in which E is the energy of the system. The two forms of the wave function, Ψ and ψ , used in the course of the equation accordingly represent different conceptions, in that Ψ conventionally includes both the time and the space dimensions of the function, whereas ψ is the amplitude function.

For the expression of the variation of ψ with spatial coordinates, three such coordinates are necessary for each electron in the atomic system, i.e. six spatial coordinates, all of them different, for an atomic system containing two electrons. Accordingly, the variation of ψ must be a mathematical rather than an ordinary spatial one.

For a single-electron atom, the 'spatial' variation can be expressed by Schrödinger's equation:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0,$$

in which V is the potential energy of the electron (varying with its position), m is its mass, and E is the total energy, which is constant for a given value of ψ . It is known from the mathematical form of the equation that finite, single, and spatially continuous values for ψ are only possible for discrete values of E , which have been identified with the electronic energy levels or with the orbits in the Bohr atom; and it can be shown that the equation derived wave-mechanically for the n th value of E , in the series of possible values of E for the hydrogen atom, is identical with Bohr's equation representing the total energy value for an electron in the n th orbit, i.e. the total energy required to bring the electron from this orbit to infinity.

These abstract wave functions, which are probably only mathe-

matical concepts having no real existence as waves but expressing the type of localization which occurs in real wave packets lying in atomic fields, can be applied directly to the extension of electrons in real space. It can be shown that if the particle-wave representing an electron is regarded as being capable either of being dispersed through space or of being progressively concentrated or localized as a wave packet, then a derived wave function—the density distribution or probability function—based on and equivalent mathematically to the product of ψ and its conjugate,[†] can be obtained which gives the concentration or density of the ‘electron cloud’ in ordinary space or, expressed somewhat differently, the probability of the occurrence of a point-electron at a given point in space. This probability is appreciable only within limited regions known as orbitals from their analogy to Bohr orbits, the probability of occurrence outside an orbital, although finite, being virtually zero. The spatial reality of the form of orbital indicated by probability functions receives striking confirmation from the fact that the experimentally determined geometry of directed valency bonds, and of molecular structure generally, agrees with that derived wave-mechanically.

Geometry of the Wave-Mechanical Atom

As has already been stated, the discontinuous and special values of E which allow the solution of the Schrödinger wave equation for any extranuclear electron are wave-mechanically permissible energy levels for that electron. These energy levels or shells, which are called orbitals, can, as before, be classified into main level groups (K , L , M , etc.) containing subsidiary levels (s , p , d , etc.). The s orbitals are symmetrically disposed, as spherical shells, about the nucleus and occur singly (one for each of the K , L , M , etc., levels); but the higher subsidiary orbital classes, from p orbitals onwards, occur in groups in each of the L , M , and higher main levels and have, within each group, axes which possess directional characteristics with respect to the axes of other members of the group. Accordingly, each individual orbital requires for its full identification firstly, the order of its main level, secondly, the nature of its subsidiary level, and thirdly (save for s orbitals), its directional characteristic; and, since each individual electron in the atomic system may have a positive or a negative spin,

[†] The density distribution function can, more simply, be viewed as being given by ψ^2 .

each electron will, as before, have four quantum numbers, one of which refers to the sense of its spin. It should be noted, however, that the existence of still further subdivision in energy levels, linked with the possibility of more than four quantum numbers, as in the more complicated forms of the wave equation with more than three coordinates, is not impossible and is indeed to some extent borne out by the superfine structure of atomic spectra under conditions of very high dispersion.

On the basis of three non-spin quantum numbers, the Pauli exclusion principle gives the following orbitals† in the first three main levels, the general pattern and the structure both in these and in higher main levels being as already given in Table 3.

TABLE 4

<i>Main level</i>	<i>Orbital content</i>		
	$l = 0$	$l = 1$	$l = 2$
<i>K</i> (or $n = 1$)	<i>s</i>	—	—
<i>L</i> (or $n = 2$)	<i>s</i>	p_x, p_y, p_z	—
<i>M</i> (or $n = 3$)	<i>s</i>	p_x, p_y, p_z	$d_x, d_y, d_{x+y}, d_{x+z}, d_{y+z}$

Each of these orbitals can be either unoccupied or occupied by a single electron or by an electron pair with opposed spins. It is usual to denote the order of a subsidiary orbital by a number corresponding with that of its main level: thus the *s* orbital in the first or *K* shell is known as a 1*s* orbital, while that in the *L* main level is a 2*s* orbital (similarly 3*s*, 3*p_x*, etc.). The operation of the Pauli exclusion principle causes *s* orbitals to occur singly, *p* orbitals in sets of three, *d* orbitals in sets of five, and *f* orbitals in sets of seven.

It is important to note that each of these orbital types (*s*, *p*, *d*, etc.) has characteristic geometrical properties, irrespective of the main level in which it occurs. The characteristics of *s* orbitals can be most precisely calculated in the case of the hydrogen atom, which contains a single extranuclear electron occupying, in the ground state, the 1*s* orbital. It is found that the wave function representing the distribution of this electron in the ground state is spherically symmetrical with respect to the nucleus; and it can be shown that the probability of the occurrence of the electron in any spherical shell of radius *r*

† The directional characteristics of the *p* and *d* orbitals, which are largely based on Pauling's work, are dealt with in greater detail below.

and thickness dr rises to a maximum for a value of r which is identical with the radius of the Bohr orbit for this electron. The maximum-probability region for such an electron is thus a spherical shell having the nucleus at its centre, all points in this spherical surface having equal probabilities.

This type of symmetry holds for all s orbitals, e.g. for the doubly occupied $1s$ orbital in helium ($Z = 2$) and for the $1s$ and $2s$ orbitals in lithium and beryllium ($Z = 3$ and 4), although the characteristics are progressively more difficult to calculate as the atomic number scale is ascended and have largely to be inferred from the non-directional character of s -bonds; but, from boron onwards, extra-nuclear electrons begin to occupy, in the ground state, orbitals (p , d , f , etc.) which are no longer spherically symmetrical about the nucleus but which have a directional tendency along radial axes originating in the nucleus. These directed orbitals occur, as already mentioned, in sets of three, five, and seven. The radial direction of any single member of such a set is indeterminate; but the axes (passing through the nucleus) of the individual orbitals in a given set have definite angular directions with respect to the axes of the other orbitals of the set. It is these radially directed types of orbital, or hybrids involving these orbitals (see later), which are responsible for directed covalent bonds in chemical compounds.

In the case of p orbitals, which constitute the simplest directed type, the three orbitals of each set have been shown by Slater† and by Pauling‡ to be directed along three Cartesian coordinates with the nucleus at the origin. It is thus possible to designate the three p orbitals as p_x , p_y , and p_z , in which x , y , and z have their usual meanings as rectangular spatial coordinates.

A set of p orbitals, for an atom in an uncombined state, is shown diagrammatically in Fig. 4, in which the large circles represent a plane section of an envelope or shell. To avoid confusion the p_y orbital is indicated by dotted lines and the p_z orbital has been omitted, since its axis is at right angles to the plane of the paper. The small dark circle represents the nucleus. It may be noted that the length of the radius vector r is a measure of the electron density at that point of the orbital, or of the probability of the occurrence

† J. C. Slater, *Phys. Rev.* 1931, **37**, 481.

‡ L. Pauling, *J. Amer. Chem. Soc.* 1931, **53**, 1367; L. Pauling and J. Sherman, *ibid.* 1937, **59**, 1450.

of a point-electron at that point. Accordingly, since there is, in covalent bond formation, a trend towards maximum electronic overlap between the atoms involved in the bond, it will be seen that bonds involving a set of three p orbitals should be mutually at right angles to one another.

The shape and the direction of the five d orbitals with respect to

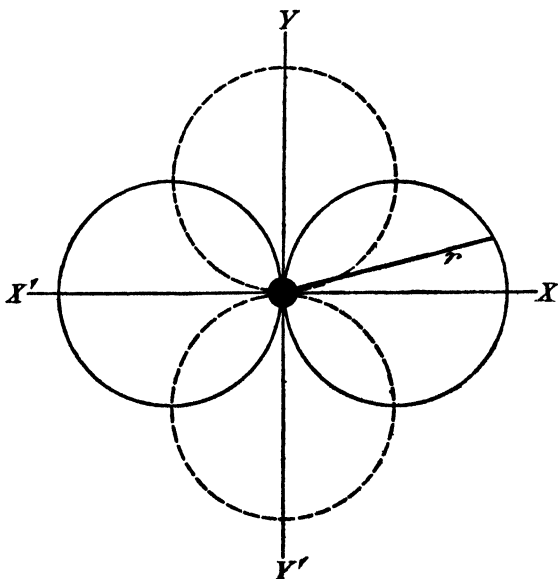


FIG. 4.

one another are more complicated since, according to Pauling's treatment,[†] each d orbital has a maximum in four directions and the orbitals are not mutually equivalent. Pauling classifies them into d_x , d_z , d_{x+y} , d_{x+z} , and d_{y+z} orbitals and gives four-lobed radial distribution graphs in which the preferred directions lie either along or symmetrically between orthogonal coordinates. More simply,[‡] the set of five d orbitals may be viewed as being directed along the slant edges of a pentagonal pyramid with the nucleus at the apex. From the standpoint of the formation of covalent bonds, the use of pure d orbitals is rare, although hybrids involving orbitals of this order are of considerable importance. Directed orbitals and directed bonds are dealt with further in a later section.

[†] L. Pauling, loc. cit., p. 1387.

[‡] G. E. Kimball, *J. Chem. Phys.* 1940, 8, 194.

It may be noted that the physical picture of a wave-mechanical atom has been particularly clearly discussed by Bowen.[†] If an atom is viewed as a system of 'real' three-dimensional standing waves, then the various types of orbitals are to be regarded as antinodes inside this standing wave system. The change in the atomic shape as the electronic energy is increased is most easily visualized for a single electron atom, i.e. hydrogen. In its fundamental vibration mode,

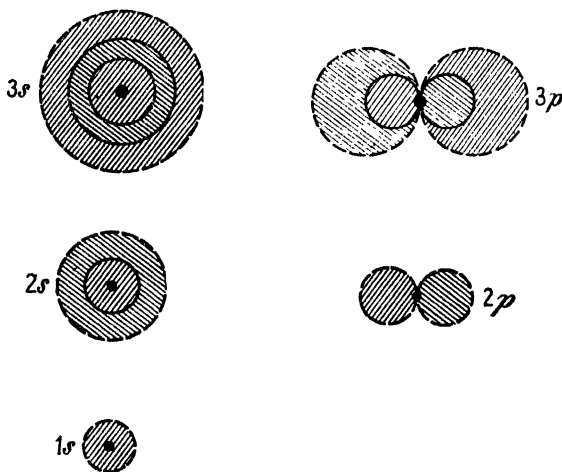


FIG. 5.

corresponding with the ground or $1s$ state, the standing wave representing this electron is a three-dimensional sphere having a nodal boundary and a two-dimensional spherical-shell antinode (maximum $\psi^2 dV$ region) at the Bohr-radius distance, r , around the nucleus.

Higher-energy electronic states result in a modification of the electron cloud, accompanied by the formation of harmonics and of new nodes and antinodes in the electron-wave system: thus the $2s$ and the $3s$ states give rise respectively to two and to three spherical-shell nodes, symmetrical about the nucleus, as shown in Fig. 5, in which the change in the direction of the shading indicates a change in phase; but, in addition to this repetition of orbital type, energy increase may cause a change in the geometrical form of the electron standing wave and in that of its nodes, e.g. the s vibrational form may be changed into a p form of standing wave, consisting of three-dimensional spherical lobes of opposite-phased waves (with two-dimensional

[†] E. J. Bowen, *Ann. Reports Chem. Soc.* 1943, 40, 12.

spherical-shell nodes) on opposite sides of the nucleus, as is indicated in the figure for the $2p$ state. Further, the p series will also have harmonics of similar type, $3p$ being a harmonic of $2p$.

Bowen regards p orbitals as being characterized by an additional node at the atomic nucleus, the most important central nodal type being planar. A node of this type is shown by $ABCD$ in Fig. 6. The p orbitals in each main level, of course, occur in sets of three (p_x , p_y , and p_z) at right angles to one another, as already described.

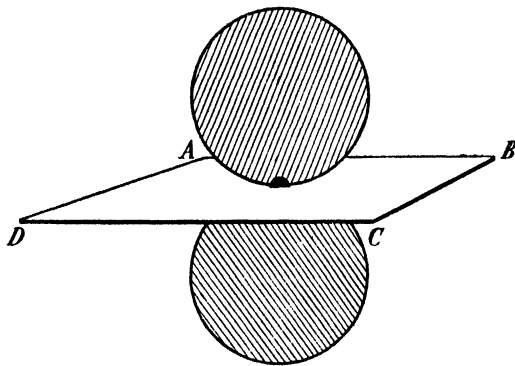


FIG. 6.

The actual passage from one vibration mode to another, as an atom is raised in energy by excitation, will be governed by 'permitted' or 'forbidden' transitions. Thus, $s \rightarrow p$ transitions are in general permitted, whereas $s \rightarrow s$ transitions are forbidden except under special conditions. For further details reference should be made to Bowen's article.

THE ELEMENTS

The electronic configuration for the series of elements in their normal or ground state is given in Table I of the Appendix, the position of each new electron added as the atomic number increases being indicated by an asterisk for inner-shell additions.

It will be seen, firstly, that similar elements have similar electronic structures in their outer shells and, secondly, that several series occur in which, as the atomic number progressively increases, the outer electronic structure remains the same, the added electron falling into an uncompleted inner shell. This gives rise to the so-called transition series of elements, namely, to elements of similar properties but of

progressively increasing atomic number. Instances of this are given by the rare earths and by the metals of the iron, of the palladium, and of the platinum groups; but, as is evident from the table, transition series from this standpoint are far wider than the three classical series (Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt) in Group VIII of the periodic system. A further discussion is omitted for reasons of space.

Isotopically Simple and Complex Elements

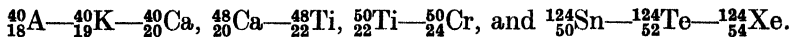
The elements, as they occur naturally, may be homogeneous or they may consist of mixtures of isotopes, i.e. of atoms of the same atomic number but of different mass numbers.

Of the stable elements in the periodic system, twenty-two (Be, F, Na, Al, P, Sc, V, Mn, As, Y, Nb, I, Cs, La, Pr, Tb, Ho, Tm, Ta, Au, Bi, and Th) are found isotopically simple in their natural state. The remainder occur as mixtures of isotopes, the number of which, for a given element, ranges from two in the case, for instance, of lithium or boron up to eleven in the case of tin.

A list of isotopes, together with their relative abundances and the probable values of their packing fractions, is given in Table II of the Appendix.

Isobars

Since the chemical properties of an element are determined by its atomic number and not by its mass number, atoms of the same mass but of differing atomic number (arising from variation of the proton-neutron ratio, subject to the proton-neutron sum remaining constant) will correspond with different chemical elements. These elements of equal nuclear mass are known as isobars. Examples of isobars are:



Separation of Isotopes

The isolation, at any rate in reasonably large quantities, of pure individual isotopes from the natural mixture presents great difficulties in practice on account of the close correspondence of the chemical and physical properties of these isotopes, an exception to this generalization being the special case of deuterium and hydrogen, in which the abnormally large mass ratio (two to one) and the large difference in zero-point energy facilitate separation.

Small quantities of almost any isotope of sufficient relative abundance can be obtained in a pure state by means of the crossed

electrostatic and magnetic fields of the mass spectroscope. Thus Smythe and Hemmendinger† obtained separate deposits of several milligrams of the three potassium isotopes, ^{39}K , ^{40}K , and ^{41}K , and showed that the radioactivity of potassium was confined to ^{40}K . Similar small quantities of, for instance, the isotopes of lithium and of rubidium have also been isolated by a number of workers.‡

Apart from this mass-spectroscopic method, enrichment only, as distinguished from complete separation, has resulted in the great majority of cases from the application of most of the other methods which have been tried. These methods include separation by various forms of diffusion (porous wall diffusion, gravitational diffusion, and thermal diffusion), by electro-chemical means, by fractional distillation, and by chemical exchange reactions. A summary of the results obtained up to 1938 is contained in the article by O. J. Walker cited above. The enrichment obtained in a single-stage diffusion process is very small; but far more efficacious separation may be effected by employing multiple-stage diffusion§ in a closed system: for instance, Capron, Delfosse, de Hemptinne, and Taylor|| were able, in an apparatus containing fifty-one diffusion units, to prepare a considerable quantity of methane containing about 30 per cent. of ^{13}C in place of the normal 1 per cent. It may be noted that the diffusion method is specially effective in the case of neon, as was found at an early stage by Aston. Thus, Hertz and his co-workers,¶ using a fifty-stage diffusion apparatus, obtained substantially pure ^{22}Ne and, with ordinary hydrogen, both pure deuterium and pure ^1H .

Particular mention should be made of thermal diffusion, which has been employed recently by a large number of workers. In this method the gas to be separated is exposed to a temperature gradient between two parallel surfaces. Under these conditions, even if convection is reduced to a minimum by employing horizontal surfaces with the hotter surface uppermost, a concentration of the heavier molecules

† W. R. Smythe and A. Hemmendinger, *Phys. Rev.* 1937, **51**, 178.

‡ M. L. Oliphant, E. S. Shire, and B. M. Crowther, *Proc. Roy. Soc.* 1934, A **146**, 922; W. R. Smythe and A. Hemmendinger, *Phys. Rev.* 1937, **51**, 1052; W. Walcher, *Physikal. Z.* 1937, **38**, 961; E. L. Yates, *Proc. Roy. Soc.* 1938, A **168**, 148; see also O. J. Walker, *Ann. Reports Chem. Soc.* 1938, **35**, 137.

§ G. Hertz, *Z. Physik*, 1932, **79**, 108.

|| P. Capron, J. M. Delfosse, M. de Hemptinne, and H. S. Taylor, *J. Chem. Physics*, 1938, **6**, 656.

¶ H. Harmsen, G. Hertz, and W. Schütze, *Z. Physik*, 1934, **90**, 703; H. Harmsen, *ibid.* 1933, **82**, 589.

on the cooler surface occurs by a process which can be explained† by studying the transport equations. The effectiveness of this thermal diffusion is, however, greatly increased‡ if vertical surfaces

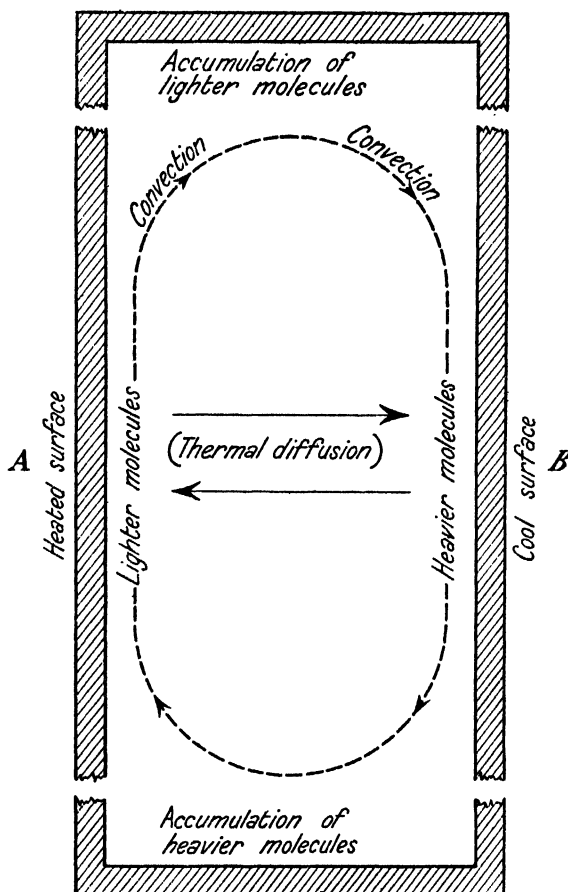


FIG. 7.

are used, in which case the heavier and the lighter molecules, concentrated by thermal diffusion on the cooler and on the hotter surfaces, are carried by convection, respectively, to the bottom and to the top, as shown diagrammatically in Fig. 7. The usual form of separation apparatus (the efficiency of which increases with its

† D. Enskog, *Physikal. Z.* 1911, **12**, 56, 533; see A. J. E. Welch, *Ann. Reports Chem. Soc.* 1940, **37**, 153.

‡ K. Clusius and G. Dickel, *Naturwiss.* 1938, **26**, 546.

height) consists of one or more long vertical tubes heated externally and containing a cooled tubular core.

Clusius and Dickel,[†] using five separation tubes in series, with a total height of 36 metres, effected a complete separation of ^{35}Cl from ^{37}Cl (in the form of HCl). Details of the atomic weight of the chlorine at the 'light' and at the 'heavy' side of the apparatus are given in Table 5. Considerable volumes (480 c.c. of ^{35}Cl and 635 c.c. of ^{37}Cl)

TABLE 5

	'Light' side (^{35}Cl)	'Heavy' side (^{37}Cl)
Atomic weight found	34.979	36.956
Atomic weight of pure isotope	34.971	36.968
Purity	99.6 per cent.	99.4 per cent.

were obtained: accordingly the thermal diffusion method appears to be of great practical interest for isotopic separation generally.

In many cases, however, a concentration of an isotope, rather than a complete separation, has been obtained. Thus Nier and Bardeen[‡] were able to increase the $^{13}\text{C} : ^{12}\text{C}$ ratio in methane to over eleven times its normal value by employing a thermal diffusion column having a total length of 74 feet (in three sections), with the external surface at about 380° and the cooled core at about 27° .

Electrochemical separation is considered in Chapter II in connexion with the preparation of heavy water.

ATOMIC WEIGHTS

The Oxygen Standard. Chemical and Physical Atomic Weights

The adoption of oxygen as a standard representing just 16 units of atomic weight led, on the subsequent discovery of the isotopic complexity of this element, to the necessity for defining more exactly what is understood by oxygen.

The basis for ordinary chemical atomic weights is the mean atomic mass of the normal isotopic mixture, which contains some ^{18}O in addition to its main component, ^{16}O , the content of other isotopes (^{17}O) being negligible. The unit of physical atomic weights, on the other hand, is not one-sixteenth of the mean weight of the mixed atoms in normal oxygen but one-sixteenth the weight of an atom

[†] K. Clusius and G. Dickel, *Z. physikal. Chem.* 1939, B 44, 451.

[‡] A. O. Nier and J. Bardeen, *J. Chem. Phys.* 1941, 9, 690.

of the ^{16}O isotope alone: consequently the chemical unit is slightly larger than the physical one; or, conversely, the atomic weight of an element on the chemical scale will, since it is expressed in somewhat larger units, be slightly less than the physical atomic weight.

Owing to the great preponderance of the ^{16}O atom in the isotopic mixture, the differences involved in expressing atomic weights in these two ways—namely, against ordinary oxygen or against ^{16}O alone—are not very great. The abundance ratio of ^{16}O to ^{18}O was found by Manian, Urey, and Bleakney† to be 514 ± 13 , which agrees well with measurements by other workers; and it is necessary to apply a conversion factor‡ of 1.000275 in correcting atomic weights from the chemical to the physical scale. This involves, for instance, a difference of about 3 in the second decimal place in the case of an element of atomic weight 100.

Determination of Physical Atomic Weights

In spite of the great precision which has been attained in the classical chemical methods of atomic weight determination, still more accurate results are in many cases obtainable by physical means. The methods employed involve:

1. The determination of the atomic masses of each of the constituent isotopes.
2. A knowledge of the isotopic abundance ratios.

The atomic masses of the constituent isotopes may be derived:

- (a) By direct mass-spectroscopic measurement.
- (b) By calculation from the packing fraction, the probable value of which can be obtained from the general packing-fraction curve if the mass number of the isotope is known to the nearest whole number.
- (c) From nuclear reaction energies.

Direct Mass-Spectroscopic Measurements

The theory and description of the mass-spectroscope fall outside the scope of the present volume, and for details reference should be made to Aston's standard work.§ In general, positive rays produced in an X-ray discharge tube or in a spark discharge and con-

† S. H. Manian, H. C. Urey, and W. Bleakney, *J. Amer. Chem. Soc.* 1934, **56**, 2600.

‡ W. R. Smythe, *Phys. Rev.* 1934, **45**, 299. An earlier factor, due to Mecke and Childs, was 1.00022.

§ F. W. Aston, *Mass Spectra and Isotopes*, Arnold & Co., London, 1933.

sisting of positively charged ions of the substance under examination are, after passage through a narrow slit, brought to a virtual focus by means of an electric field and, after further selection through a diaphragm, are spread out by application of a magnetic field into a mass spectrum in which the position of the lines is determined by the mass of the charged particles, by their charge, and by the dispersive power of the spectroscope. The lines can be photographed in the ordinary way on a photographic plate.

While it is possible to calibrate the instrument in such a way as to read off masses directly, the greatest accuracy is obtained by measuring the distance of a line due to a particle of unknown mass from a convenient, almost coincident reference line (due to an ion of known mass and charge), the distance between the two lines being very short. It should be noted that positive rays are given not only by atoms but also by ionized molecules, including the molecules of compounds: thus Aston has used doublets derived, at mass 2, from atomic deuterium and molecular hydrogen or, at mass 16, from ^{16}O and methane. Further, since multiply charged positive ions are also formed, especially in the spark discharge, by the loss of more than one electron, and since the position of a line is determined both by the mass and the charge, it is possible to use for mass determinations the almost coincident lines given by pairs such as $^{16}\text{O}^+ - ^{48}\text{Ti}^{3+}$ or $^{12}\text{C}^+ - ^{48}\text{Ti}^{4+}$ (Dempster) or mixed atomic-molecular pairs such as $^{12}\text{C}^{2+} - ^2\text{D}_3^+$ (Aston); or slightly divergent masses such as $^{16}\text{O}^+$, against mixed $^{63}\text{Cu}^{4+}$ and $^{65}\text{Cu}^{4+}$ (which give lines at 15.75 and 16.25 spaced at almost equal distances on each side of the oxygen line), may be used. The accuracy obtainable is now very high. Aston's third mass-spectrograph gave isotopic weights with an accuracy up to 1 part in 100,000; but the degree of accuracy was, of course, less with the heavier elements. Very accurate mass-spectrographs, some of which are different in construction from those used by Aston, have also been described by Dempster,[†] by Bainbridge and Jordan,[‡] by Mattauch,[§] and by Bleakney and Hipple.||

The relative abundance of the various isotopes is estimated by determining the relative opacity of the different isotopic lines, on

[†] A. J. Dempster, *Proc. Amer. Phil. Soc.* 1935, **75**, 762.

[‡] K. T. Bainbridge and E. B. Jordan, *Phys. Rev.* 1936, **50**, 282.

[§] J. Mattauch, *ibid.*, p. 617.

|| W. Bleakney and J. A. Hipple, *ibid.* 1938, **53**, 521.

the assumption that the amount of silver liberated from the sensitive silver salt is, for ions of approximately the same mass (which is the case with isotopes), directly proportional to the number of impinging particles. This photometric technique has been worked out in such a way as to give a high degree of accuracy; but, as an alternative, the relative number of positive particles corresponding with a given isotope can be counted electrostatically by measuring the total charge entering a Faraday cylinder during a standard time interval.† This method was actually used in early positive-ray analysis by Sir J. J. Thomson and has also been employed by Dempster, but most of Aston's measurements of abundance ratios have been made photometrically.

Given the exact isotopic weight and the abundances of the various constituent isotopes, the estimation of the atomic weight of the normal element becomes a simple arithmetical operation.

Use of the Packing Fraction

It is usually sufficient merely to determine the masses of the various isotopes to the nearest integer (i.e. the integral isotopic mass numbers) and their relative abundance, and to derive the exact isotopic weight by reading off the value of the packing fraction from the general packing-fraction curve. The packing correction can obviously be applied either to each isotope separately, or a mean (or, if necessary, a 'weighted') value of the fraction can be used to correct the mean isotopic mass.

For clearness two numerical examples are given. Lichtblau‡ found the abundance ratio of the two isotopes of europium, of mass numbers 151 and 153, to be $^{151}\text{Eu}/^{153}\text{Eu} = 0.963$. The uncorrected mean mass on the physical scale is thus 152.019. From the position of the isotopes on the packing-fraction curve, taking Dempster's values, the mean packing fraction should be -2×10^{-4} , giving, for a mass of about 152, a mean defect of 0.030. We thus have:

Mean uncorrected mass	.	.	.	152.019
Packing-fraction correction	.	.	.	- 0.030
Physical atomic weight ($^{16}\text{O} = 16$)	.			151.989
Chemical atomic weight	.	.	.	151.95

This agrees reasonably well with the value (151.96), due to Baxter

† F. W. Aston, *Mass Spectra and Isotopes*, p. 89.

‡ H. Lichtblau, *Naturwiss.* 1939, 27, 260.

and Tuemmler,[†] for the chemical atomic weight determined directly in the ordinary way.

As a more complicated example, taken from one of Aston's papers,[‡] the relative abundance of the various isotopes of krypton are as follows:

Mass number	78	80	82	83	84	86
Percentage abundance	0.42	2.45	11.79	11.79	56.85	16.70

These figures give a mean uncorrected mass of 83.857, which, when corrected for a mean packing fraction of -8.8×10^{-4} , gives an atomic weight of 83.783 on the physical scale or 83.77 on the chemical scale. This is slightly higher than the accepted atomic weight (83.70), and Aston, in a later paper,[§] considers that his earlier estimates of the abundances of some of the even isotopes are too low, but the example serves to show the method of calculation.

Isotopic Weights from Nuclear Reaction Energies

A large number of nuclear reaction energies have now been measured with an accuracy which is high if the limits of uncertainty are viewed from the standpoint of their small mass equivalence: accordingly, this method gives highly accurate isotopic weights provided that trustworthy values are known for the atomic weights of a few key elements, which can be used as constants for the determination of the atomic masses of other elements connected with them by known transmutation reactions. It may be mentioned that among these simple key elements the standardization of the atomic weight of ⁴He, which is a frequent component of nuclear reactions, has been the subject of considerable work,^{||} since, in spite of its importance, the agreement between the values obtained by various methods is not particularly good. Its most probable value for the neutral helium atom appears to be 4.00389 ± 0.0007 on the physical scale (¹⁶O = 16), corresponding to 4.0028 on the chemical scale (O = 16). This is considerably higher than the mass-spectroscopic value of 4.00136 (Aston) on the ¹⁶O scale.

The transmutation reactions involved in the estimation of isotopic

[†] G. P. Baxter and F. D. Tuemmler, *J. Amer. Chem. Soc.* 1938, **60**, 602.

[‡] F. W. Aston, *Proc. Roy. Soc.* 1930, **A 126**, 521.

[§] F. W. Aston, *ibid.* 1937, **A 163**, 401.

^{||} See, for instance, H. Bethe, *Phys. Rev.* 1935, **47**, 633; also M. L. E. Oliphant, A. E. Kempton, and Lord Rutherford, *Proc. Roy. Soc.* 1935, **A 150**, 241.

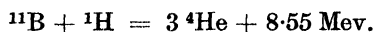
weights may be induced by bombardment with suitable energy quanta (γ -rays) or with material particles (neutrons, protons, deuterons, etc.). The method of calculation is simple and similar in each case, since it depends on the conservation of energy-mass on each side of the equation, the transmutation energy or other energy terms being expressed as their mass equivalent.

As a simple case, a calculation of the mass of the neutron may be considered. When deuterium is bombarded with high-energy γ -radiation, the deuterium nucleus is split into a proton and a neutron, the threshold energy value for the disintegration, according to the calculations of Chadwick, Feather, and Bretscher, being 2.26 Mev. Since 1 Mev. is equivalent to 0.00107 atomic mass units, this threshold energy value corresponds with 0.0024 units of mass. Accordingly, if this mass equivalent and the well-established values for the masses of the deuterium nucleus and the proton are inserted in the equation:

$$\begin{array}{ccccccc} {}^2_1\text{D} & + & h\nu & = & {}^1_1\text{H} & + & {}^1_0\text{n} \\ (2.0142) & & (0.0024) & & (1.0076) & & \end{array}$$

it will be found that the mass of the neutron, on the ^{16}O scale, comes out as 1.0090.

Similarly, as an instance involving particulate bombardment, it has been found† that the α -particles resulting from the proton bombardment of the boron isotope ^{11}B in the reaction



have a mean energy of 2.85 ± 0.03 Mev., corresponding, for the three particles, with 8.55 Mev., as inserted in the equation, or with 0.0091 mass units. On the basis (used by the authors cited) of a value of 4.0034 for ${}^4\text{He}$:

$$^{11}\text{B} = 3(4.0034) + 0.0091 - 1.0081 = 11.0112.$$

Some further examples of nuclear reaction energies and of the atomic weights calculated from these are given in Tables 6 and 7, the summaries being in each case due to Wilson.‡ The atomic weights are on the physical scale, and all energies are expressed in atomic mass units.

It may be noted that in making calculations of the above type it is usually more convenient to employ ordinary isotopic weights, representing the masses of the complete atoms, rather than nuclear

† Bethe, loc. cit.; Kirschner, *Phys. Z.* 1933, **34**, 897.

‡ H. A. Wilson, *Proc. Roy. Soc.* 1935, A **152**, 497.

weights representing the masses of the nuclei only, since the number of electrons in the system (and therefore their mass) remains constant and accordingly cancels out from both sides of the mass-energy equation.

TABLE 6

${}^2\text{D}$	+	${}^2\text{D}$	=	${}^3\text{H}$	+	${}^1\text{H}$	+	0.00426 atomic mass units
${}^2\text{D}$	+	${}^2\text{D}$	=	${}^3\text{He}$	+	${}^1_0\text{n}$	+	0.00285
${}^6\text{Li}$	+	${}^1\text{H}$	=	${}^4\text{He}$	+	${}^3\text{He}$	+	0.00386
${}^6\text{Li}$	+	${}^2\text{D}$	=	$2\,{}^4\text{He}$	+			0.02368
${}^6\text{Li}$	+	${}^2\text{D}$	=	${}^7\text{Li}$	+	${}^1\text{H}$	+	0.00537
${}^7\text{Li}$	+	${}^1\text{H}$	=	$2\,{}^4\text{He}$	+			0.01831
${}^7\text{Li}$	+	${}^2\text{D}$	=	$2\,{}^4\text{He}$	+	${}^1_0\text{n}$	+	0.0157
${}^9\text{Be}$	+	${}^1\text{H}$	=	${}^8\text{Be}$	+	${}^2\text{D}$	+	0.00051
${}^9\text{Be}$	+	${}^1\text{H}$	=	${}^6\text{Li}$	+	${}^4\text{He}$	+	0.0022
${}^9\text{Be}$	+	${}^2\text{D}$	=	${}^7\text{Li}$	+	${}^4\text{He}$	+	0.00775
${}^9\text{Be}$	+	${}^2\text{D}$	=	${}^8\text{Be}$	+	${}^3\text{H}$	+	0.0048
${}^9\text{Be}$	+	${}^2\text{D}$	=	${}^{10}\text{Be}$	+	${}^1\text{H}$	+	0.0050
${}^9\text{Be}$	+	${}^2\text{D}$	=	${}^{10}\text{B}$	+	${}^1_0\text{n}$	+	0.0053
${}^9\text{Be}$	+	${}^1_0\text{n}$	=	${}^8\text{Be}$	+			0.0016
${}^{11}\text{B}$	+	${}^1\text{H}$	=	$3\,{}^4\text{He}$	+			00.091
${}^{11}\text{B}$	+	${}^1\text{H}$	=	${}^8\text{Be}$	+	${}^4\text{He}$	+	0.0092
${}^{10}\text{B}$	+	${}^1_0\text{n}$	=	${}^7\text{Li}$	+	${}^4\text{He}$	+	0.0021

TABLE 7

 ${}^{16}\text{O} = 16$

Element	Calculated atomic weights		
	Wilson (He = 4.00342)	Bethe	Oliphant, Kempton, and Rutherford
${}^1_0\text{n}$	1.00833	1.0085	1.0083
${}^1\text{H}$	1.00791	1.00807	1.0081
${}^2\text{D}$	2.01416	2.01432	2.0142
${}^3\text{H}$	3.01626	3.01610	3.0161
${}^3\text{He}$	3.01709	3.01699	3.0172
${}^4\text{He}$	4.00342	4.00366	4.0034
${}^6\text{Li}$	6.01634	6.01614	6.0163
${}^7\text{Li}$	7.01720	7.01694	7.0170
${}^8\text{Be}$	8.00726	—	8.0071
${}^9\text{Be}$	9.01393	9.0135	9.0138
${}^{10}\text{Be}$	10.01520	—	10.0149
${}^{10}\text{B}$	10.01437	10.0146	10.0143
${}^{11}\text{B}$	11.01149	11.0111	11.0110

In looking through the above tables it will be seen that certain of the isotopes listed (although these occur as common products of nuclear transformation) are not found naturally in sufficient abundance to be included in ordinary tables of natural isotopes. It may

also be noted that Wilson,[†] with the object of reducing the number of necessary 'key' atomic weights, has calculated the atomic weights of various light elements directly from the energy of formation and from the masses of the neutrons and protons contained in the atoms.

Nuclear reaction energies find particular application in the determination of the atomic weights of artificial radioactive elements, especially those of short life. As an example, Lawrence[‡] has calculated the atomic mass of radio-sodium, ^{24}Na , which can be formed by the bombardment of ordinary sodium, ^{23}Na , with high-energy deuterons from a cyclotron. In such a case the mass equivalent of the kinetic energy of the bombarding particles is too high to be neglected. In an energy-mass balance of the reaction as induced by deuterons of an energy of 2.15 Mev., the various terms on each side of the disintegration equation (using the chemical O = 16, mass scale) are as follows:

$$\begin{array}{ccccccc}
 ^{23}\text{Na} & + & ^2\text{D} & + & \text{k.e. of } ^2\text{D} & = & ^{24}\text{Na} + ^1\text{H} + \text{k.e. of } ^1\text{H} + \text{k.e. of } ^{24}\text{Na} \\
 22.999 & & 2.0136 & & 0.0023 & & 1.0078 & 0.0066 & 0.0006 \\
 & & & & (2.15 \text{ Mev.}) & & & (6.2 \text{ Mev.})
 \end{array}$$

From these figures $^{24}\text{Na} = 24.000$ on the chemical scale.

Energy-mass balances may also be used for the natural radioactive elements. Western and Ruark[§] have calculated in this way the isotopic weights of the radioactive elements by starting with the well-established atomic weights of the lead isotopes and, working upwards, by adding the mass and the mass-equivalent of the energy change for each disintegration stage. For a list of such isotopic weights reference should be made to Western and Ruark's paper. The calculated atomic weight of radium (226.02 on the chemical scale) is 0.05 unit higher than the chemically determined value, and that for uranium is also somewhat higher than the accepted value.

A list of the atomic weights of isotopes and of the natural elements is included in Tables II and III of the Appendix.

CHEMICAL BONDS AND THE STRUCTURE OF MOLECULES

This fundamentally important subject can only be dealt with in outline, and for a fuller treatment reference should be made to

[†] H. A. Wilson, *Proc. Roy. Soc.* 1936, A 154, 560.

[‡] E. O. Lawrence, *Phys. Rev.* 1935, 47, 17.

[§] F. Western and A. E. Ruark, *J. Chem. Phys.* 1933, 1, 717; S. Meyer, *Wien. Ber.* (ii A), 1928, 137, 647.

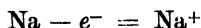
standard works on chemical bonds such as those of Sidgwick† or Pauling.‡

According to the electronic theory of valency, as developed by G. N. Lewis, Kossel, Langmuir, and others, chemical bonds may be of two extreme types, namely, electrovalent (often called ionic) or covalent. It should, further, be noted that atoms can be linked by van der Waals forces and that a special type of linkage, the metallic bond, exists in the metals.

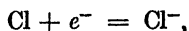
An electrovalent bond is dependent on the coulombic attraction between two oppositely charged atomic or molecular entities. These entities are usually separate ions, e.g. Na^+ and Cl^- in sodium chloride; but factors such as the separation of electrical charge (presence of a permanent electric dipole) in a molecule which is neutral when considered as a whole may also give rise to internal or external ionic linkages.

The formation of the simplest form of ions is due to the ease with which the external or 'valency' orbits of the metals and of the non-metals respectively lose or take up electrons. During this process the electronic structure of the atoms usually passes into that of an inert gas type, which corresponds with maximum stability; and, since the external shell of all the inert gases, save helium, contains eight electrons, the transition is often referred to as the 'completion of the octet'.

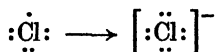
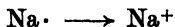
The formation of a sodium ion and of a chlorine ion may thus be represented by the processes:



and



or, according to the conventional electronic nomenclature, in which the usual symbols for the elements include all the extranuclear electrons except those in the valency shells, which are indicated by dots:



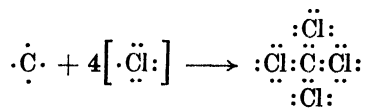
The formation of an ionic bond between a neutral sodium and a neutral chlorine atom is sometimes viewed as being preceded by the transfer of one electron from the former to the latter, with produc-

† N. V. Sidgwick, *The Electronic Theory of Valency*, Clarendon Press, 1927.

‡ L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1939.

tion of the respective, oppositely charged ions; but the bond cannot, of course, be formed until the ions have been produced.

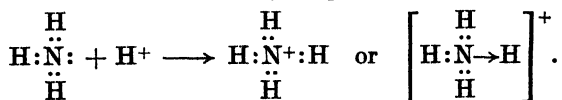
In a covalent linkage, on the other hand, a process involving some form of electron sharing (usually the sharing of an electron pair) takes place. This may be illustrated by the formation of carbon tetrachloride:



Covalent links involving the sharing of a single electron, as in the hydrogen molecule-ion, $\text{H}\cdot\text{H}^+$, and three-electron bonds are also known; but each of these bond types is rare. Ordinary electron-pair bonds in which the sharing, between two atoms, of more than one electron pair occurs are, of course, common and correspond with double and triple linkages. Such bonds are written $\text{C}::\text{C}$ and $\text{C}:::\text{C}$.

Although a shared electron pair has to be considered as shared evenly between the two linked atoms, for counting charge and certain other purposes one electron of the pair is conventionally assigned to each of the sharing atoms. Accordingly, a special type of linkage, called by Lowry† the semi-polar bond, occurs if both of the shared electrons are derived from the same atom, since in this case the donor atom acquires a positive charge, and the acceptor atom a negative one, on grounds of the net loss or gain, respectively, of an electron if these are counted by the conventional system given above. The bond is thus a double one of mixed type, containing a single covalent linkage by reason of the shared electron pair and a single electrovalent link by reason of the opposed charges. Semi-polar bonds are called by Sidgwick coordinate links, since they represent the type of linkage responsible for coordination compounds of Werner.

A simple example of the semi-polar link is given by the formation of the ammonium ion by the donation of the unshared electron pair of ammonia to an electron-free hydrogen ion:

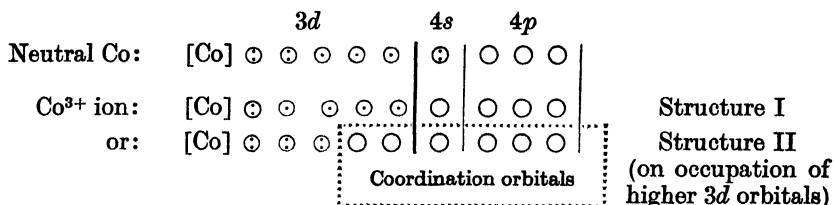


The direction of transfer of the electrons from the donor to the acceptor is often indicated by means of an arrow, as in the representation of the alternative structure for the ammonium ion in the above

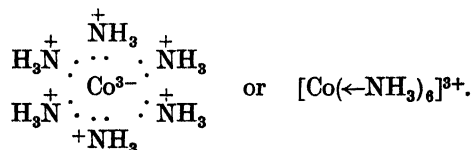
† T. M. Lowry, *Trans. Faraday Soc.* 1923, 18, 285.

equation; and it will be seen that the donor atom must possess at least one unshared pair of electrons (a single unshared electron pair is called a 'lone pair') and, secondly, that the resulting compound will often have a permanent electric dipole.

Coordination assumes special importance with elements of the transition series which possess, immediately within the normal (*s*) valency orbital, vacant or singly occupied *d* orbitals available for electron acceptance from a suitable donor. Thus, the cobaltic ion, which differs from a neutral cobalt atom by having acquired a triple positive charge by losing three electrons from *s* and *d* orbitals of approximately equal energy (see Fig. 3), namely, two from the 4*s* orbital and one from a practically equivalent 3*d* orbital, has the electronic structure indicated by I or II.



Since electron transition between orbitals of similar energy readily occurs, the normal structure (I) may be regarded as easily capable of passage into structure II, in which the two 3*d* orbitals, in addition to the single 4*s* and all the 4*p* orbitals, are completely vacant for electron acceptance. It will be explained later that six 'hybrid' orbitals, involving all the *d*, *s*, and *p* orbitals enclosed in dotted lines in structure II, are very often concerned in the formation of coordination compounds, Co³⁺ giving, for instance, with ammonia, the compound:



Such a compound is—as will be seen on counting electrons and as, of course, follows from the union of the triply charged cobaltic ion with the neutral ammonia molecule—electrovalently trivalent like the original ion, the central atom having a formal charge of -3 and the nitrogen of each of the six ammonia molecules a charge of $+1$, as a result of electron acceptance and donation.

The geometry of coordination compounds will be dealt with in a later section; but it should be noted that the semipolar or coordinate link, although a double bond by virtue of being both a covalent and an electrovalent linkage, is equivalent to a single covalent bond from a stereochemical standpoint, e.g. it does not prevent free rotation like an ordinary double bond.

Pauling makes a distinction between the coordination number of the central atom and the covalency. The former is the number of atoms or of atomic groups attached to the central atom. The latter is the number of single covalent bonds formed by this atom. In the case of polyvalent groups, these numbers may be different.

ELECTRONIC STATES IN MOLECULES

Electronic configurations in covalent molecules may be considered from two distinct standpoints, which are known respectively as the method of molecular orbitals and the method of atomic orbitals. The molecular orbital mode of visualizing electronic energy states in molecules is considered briefly in the next section and is merely an extension of the corresponding treatment of electron energy levels in atoms. This method can be applied equally well to electrons considered from a particle or a wave aspect.

In the method of atomic orbitals, on the other hand, the spatial distribution and energy states of individual electron waves in the component atoms of a covalent molecule are considered wave-mechanically, the treatment being applied to those orbitals which are involved in bond formation. This treatment leads to a theory of the nature of the covalent bond based on the phenomenon of resonance as well as to a derivation of specific orbital shapes which accounts for various types of directed valency bonds and for the observed geometrical arrangement—which can be deduced by measuring interatomic distances and valency angles empirically—of individual atoms in covalent molecules.

Molecular Orbitals

According to the Mulliken-Hund treatment of orbitals in covalent molecules, the association of the constituent nuclei is viewed as being accompanied by the building up, around the nuclear complex, of new molecular orbitals occupied by electrons from all the atoms involved in the formation of the molecule. Thus, although there may

be, particularly in complex molecules, a probability of the continued closer association of certain electrons with their parent atom, the new configuration will, in simple molecules, correspond with a 'pooled' electronic structure governed by regularities and laws—including the Pauli principle—very similar to those which control and limit the formation of electronic shells around a simple atomic nucleus.

This aspect of molecules leads to the spectroscopic nomenclature and consequently to a convenient method of denoting formally the electronic state of a molecule; but it does not readily lend itself to a simple treatment of the nature of the covalent bonds themselves.

A fuller discussion of electronic configurations in molecules is omitted for reasons of space.† One point may, however, be noted. Whereas molecules containing an odd number of electrons necessarily have an unpaired electron and are therefore paramagnetic, molecules containing an even number of electrons can exist either as a completely paired ($^1\Sigma$) and therefore diamagnetic structure or as a $^3\Sigma$ structure in which two of the even number of electrons occupy different levels, in which case the total electronic spin is unbalanced and the molecule is paramagnetic. This occurs, for instance, in the ground state of the oxygen, nitric oxide, and NO_2 molecules. The point is dealt with further on pp. 69–74.

NATURE OF THE COVALENT BONDS

The Concept of Resonance

The electronic theory of valency offers no explanation for the stability of the covalent bond, which is expressed formally as a sharing of electrons by the atoms involved without the advancement of any reason why this process of electron sharing should give rise to an often very strong chemical link.

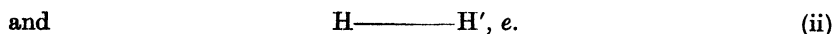
It is evident that some form of energy fall in the system occurs during the formation of the bond. This is most readily approached by way of the concept of resonance and by considering the interaction of the orbital electrons (regarded as waves) of the individual atoms involved in the bond.

The phenomenon of resonance is most simply illustrated by the Heitler–London treatment‡ of the hydrogen molecule-ion ($\text{H}\cdot\text{H}$)⁺,

† A convenient summary, including the conventional method of expressing molecular states, is given in Chapter II of S. Glasstone's *Recent Advances in General Chemistry* (J. and A. Churchill).

‡ See Pauling, *Nature of the Chemical Bond*, p. 17.

although this contains an unusual (single-electron) bond. The single electron, the sharing of which causes the bond, may be regarded as possessing a probability of occurring in the atomic orbitals of either of the linked atoms. Thus, if the two hydrogen nuclei are distinguished as H and H', the system can have the alternative configurations:

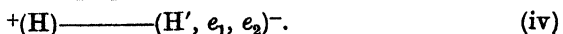
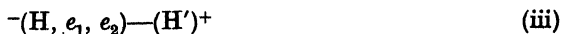


It is possible, for this simple molecule, to calculate the energy content of each of the above structures. This energy is, in this case, equal for the two structures, from which it follows quantum-mechanically that each structure has an equal probability of occurrence. It is found, however, that the actual energy content of the hydrogen molecule-ion is less, by some 50–60 kg.-cals. per mole, than the energy of either of these component configurations, i.e. if ψ_1 and ψ_2 are the wave functions corresponding with structures (i) and (ii), these wave structures interact by what has come to be known as resonance (from a formal analogy to the resonance of coupled oscillators) to form a lower-energy hybrid system, having a wave function ψ , corresponding to the normal state. ψ can be expressed additively in terms of ψ_1 and ψ_2 by an equation of the type:

$$\psi = a\psi_1 + b\psi_2,$$

where the coefficients a and b represent the relative contributions of structure (i) and structure (ii) to the normal state. The fall in energy which is brought about by this resonance is called the resonance energy and is a measure of the stability of the bond. As a slight modification in the above aspect, a point-electron may be viewed as resonating between the two hydrogen nuclei with a frequency which is given by Planck's equation: $E = \nu h$. Resonance energy of this type is accordingly sometimes called electron exchange energy.

Similarly, a neutral hydrogen molecule, H: H, which contains the more usual electron-pair bond, may be regarded as having a possibility of existence in the following four alternative configurations, in which the two electrons are distinguished as e_1 and e_2 :



In this case it can be shown that the contribution of structures (iii) and (iv) to the normal state is far less than that of structures (i) and (ii). It should be noted, further, that the actual or normal state of a resonating system is not a mere mixture of two or more isomers, as in tautomerism. The normal state corresponds with the existence of a distinct lower-energy resonance hybrid to the formation of which each of the component configurations contribute.

Resonance is a widely occurring phenomenon. It is the cause not only of ordinary covalent bond formation but also of the abnormal stability of many complex molecules, in which its presence can be recognized, for instance, by experimentally measured heats of formation which are higher than the calculated values, this higher heat of formation corresponding with a lower energy content. Thus the observed heat of formation of benzene is higher, by about 39 kg.-cals. per mole, than the value which can be calculated for the Kekulé formula of alternate single and double bonds.

The conditions obtaining in all types of resonance may be expressed formally as follows. When it is possible to set down several electronic configurations for a given system, the wave function for the system in its normal state can be expressed as a linear combination of the separate wave functions of the individual configurations, i.e.

$$\psi = a\psi_1 + b\psi_2 + c\psi_3 + \dots$$

The energy content of the hybrid resultant is always lower than that for each of the individual configurations; and the coefficients a , b , c , etc. are such that the energy of the hybrid is a minimum.

Three types of such electron-configuration hybridism occur frequently in molecular structure problems. These are:

- (i) Electron-exchange hybridization of the nature already discussed in connexion with the Heitler-London treatment of covalent bonds in the hydrogen molecule and in the hydrogen molecule-ion. This type of resonance is an essential factor of all covalent bonds.
- (ii) Orbital hybridization.
- (iii) Valence bond (e.g. single-double bond) hybridization.

Orbital Hybridization

The bond actually formed between two atoms will be that which corresponds with the condition of minimum energy, i.e. with the

greatest possible bond strength. It is frequently found that stronger bonds than are possible with pure s , p , d , etc. orbitals can be formed (usually in sets) by using hybrid orbitals, in the making of which these pure orbitals contribute as resonance components.

The individual contributions of the components to the hybrid will, as before, be those which result in the strongest bond. Thus, while a hybrid orbital involving s and p orbitals and corresponding with

$$\psi = a\psi_s + b\psi_p$$

can† conceivably vary from a pure s to a pure p orbital by variations in the relative values of the coefficients a and b , the most stable bonds will be formed if the relative value of these coefficients is such that it gives a minimum-energy value for ψ . The subject is dealt with in greater detail in connexion with the various types of covalent bonds.

Valence-Bond (Bond-Multiplicity) Hybridization

There is a considerable body of evidence—based, for instance, on abnormal bond lengths—that hybridism involving resonance between different multiples of a single bond (for instance, between single- and double-bond structures) occurs in many molecules and plays an important part in their stabilization. This is discussed further on p. 66.

DIRECTIONAL AND OTHER CHARACTERISTICS OF COVALENT BONDS

In general, each of the 'external' or valency orbitals in a given atom (namely, those occupied by the electron waves which are ordinarily concerned in covalent compound formation) is capable of forming, mainly through electron-exchange resonance, a single covalent bond. If the orbital in question is occupied by a single electron, the individual electrons of the electron pair involved will be derived one from the given atom and one from the atom with which bonding takes place. If the orbital is originally occupied by an electron pair, with the quantum-mechanical equivalent of opposed spins, both of the resonating electrons will be derived from the given atom and a dative bond will result; or the two electrons can, of course, both be supplied to an unoccupied valency orbital of the given atom by donation from the second atom. Further, since the resonance energy, which is the main cause of the bond, can be shown to increase with the overlap of the orbitals used by the two linked atoms, the tendency towards the production of a system of lowest possible energy

† L. Pauling, *J. Amer. Chem. Soc.* 1931, **53**, 1367.

(corresponding with the strongest possible bonds) will impose a trend towards a maximum possible overlap of the orbitals used.

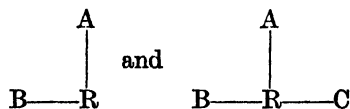
This principle of maximum orbital overlap has two important consequences. In the first place, if the degree of overlap can be increased by virtue of the special shape of a hybrid orbital compared with the form of pure orbital normally occupied by a bonding electron, then there will be a tendency towards the formation of a set of such hybrids by orbital resonance, and these hybrid orbitals will be used in place of the pure orbitals in the formation of the bonds. Secondly, if the orbital type used is such that it has directional character, this will be reproduced in the mutual directional relationships in the set of bonds thus formed by a given atom.

The directional character of the principal types of covalent bonds is summarized diagrammatically in Fig. 8. These are dealt with below, the treatment being mainly that of Pauling.

Bonds involving Pure Orbitals

s Bonds. Pure *s* bonds can have no directional nature both in view of the spherical symmetry of *s* orbitals with respect to the nucleus and of the occurrence of these orbitals singly.

p Bonds. Since *p* orbitals occur in sets of three, along rectangular coordinates with the nucleus at the origin, compounds of the types



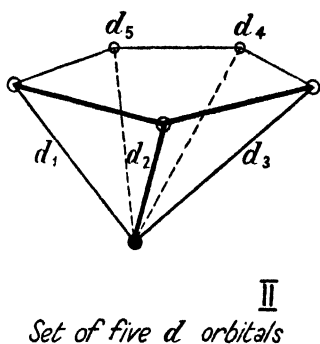
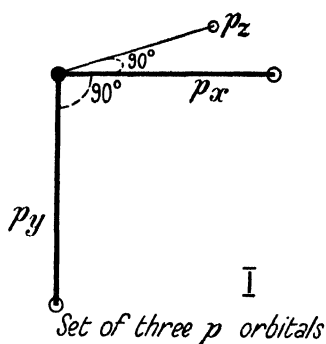
should have valency angles ARB and ARC equal to 90° , the ARC plane being at right angles to the plane containing ARB. The influence of partial ionic character in the bond in modifying this characteristic angle between sets of *p* bonds is dealt with below.

d Bonds. *d* orbitals do not seem to be well adapted, by themselves, for bond formation: consequently pure *d* bonds are rare. On the basis of Pauling's treatment,[†] each *d* orbital in the set of five has a spatially two-dimensional tendency and is difficult to visualize; but Kimball[‡] considers *d* bonds as being directed along the slant edges of a pentagonal pyramid and, for simplicity, this form has been inserted in Fig. 8.

[†] *J. Amer. Chem. Soc.* 1931, **53**, 1367.

[‡] G. E. Kimball, *J. Chem. Phys.* 1940, **8**, 194; see also H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.* 1940, **36**, 679.

SINGLE ORBITAL TYPES



HYBRID ORBITALS

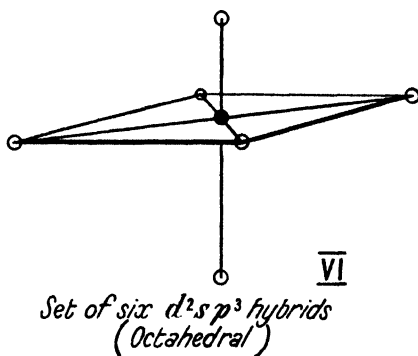
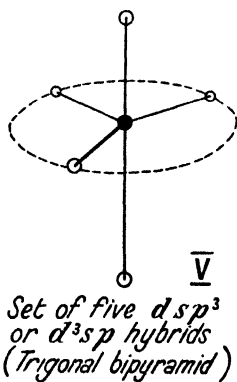
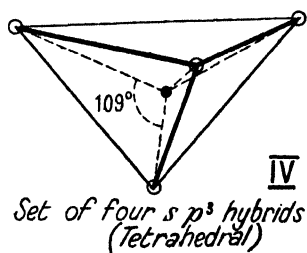
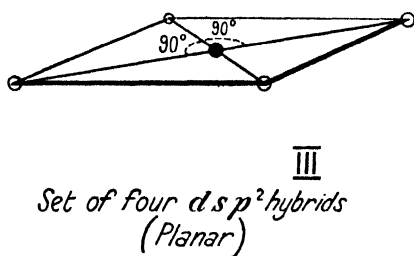
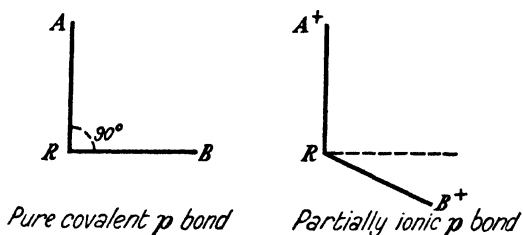


FIG. 8. Bond directions in various orbital types.

Partial Ionic Character in Covalent Bonds

It will be convenient at this point to discuss briefly ionic character in covalent bonds. Reference to p. 51 will show that it is possible for some of the component structures of a resonance hybrid (i.e. structures iii and iv in the example given) to have an ionic character. In the case of the hydrogen molecule, each of these ionic structures contributes very little (about 2 per cent.) to the normal structure.

If ionic structures contribute appreciably in sets of bonds having a directional character, distortion of the normal covalent bond angles for the particular orbital type used in the bond may occur. Thus, the rectangular rule for sets of p bonds may be modified by electrostatic repulsion, as is shown diagrammatically below, the distortion increasing with the ionic character of the bonds:



As examples of this effect, the $\text{S}-\text{H}$ bond angle in gaseous hydrogen sulphide, in which the bonds are almost purely covalent, has been found by Cross and Crawford,[†] from spectroscopic evidence,

to be about 92° , whereas the $\text{O}-\text{H}$ bond angle in water, in which the links are about 40 per cent. ionic, is 105° . Similarly, in ammonia

the $\text{H}-\text{N}-\text{H}$ angles are as high as 108° , owing to the high degree of ionic character in the $\text{N}-\text{H}$ bonds. For the reasons (more stable bonds) why these links are p bonds reference should be made to Pauling's work,[‡] on which much of the necessarily condensed treatment of the subject given in the present section is based.

Bonds involving Hybrid Orbitals

As has already been stated, the bonds actually formed between two atoms will tend to be those which correspond with the condition

[†] P. C. Cross and B. L. Crawford, *Phys. Rev.* 1935, **47**, 7; *J. Chem. Phys.* 1937, **5**, 371.

[‡] *Nature of the Chemical Bond*, Chapter II.

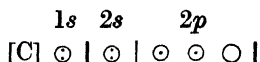
of minimum energy, i.e. with the greatest possible bond strength; and in place of using normal (*s*, *p*, *d*, etc.) orbitals it is frequently found that still stronger bonds can be formed by orbital hybridization. In this, two (or more) normal types of orbital contribute to a new composite or hybrid orbital.

s-p Hybrid Bonds. A hybrid orbital involving *s* and *p* orbitals and of the form

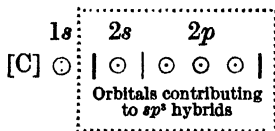
$$\psi = a\psi_s + b\psi_p$$

can† conceivably vary from a pure *s* to a pure *p* orbital by variations in the relative values of the coefficients *a* and *b*; and the most stable hybrid will correspond with the relative value of these coefficients which gives a minimum-energy value for ψ .

An important example of this type of hybridization is given by the four usual valencies of the carbon atom. This atom, in its ground state, contains in its valency or *L* shell (*n* = 2) one doubly occupied 2*s* orbital and two (out of the three) singly occupied 2*p* orbitals:



The most direct way of forming four covalent bonds corresponding with the quadrivalency of carbon would involve, firstly, a shift of one of the 2*s* electrons to the vacant 2*p* orbital, with production of the excited electronic state



(which is a commonly occurring state of carbon since sufficient energy for this excitation is usually available), followed by the formation of one 2*s* and three 2*p* bonds; but such bonds would differ from the well-known character of tetrahedral carbon bonds in their lack of mutual equivalence and in their direction, in that one would be a non-directional *s* bond of unit strength (see Table 9) and the remaining three of strength 1.732 with directions at right angles to one another. It is found, however, on calculation that the minimum energy state, or maximum bond strength, corresponds not with the use of these normal orbitals but with four hybrid (*sp*³) orbitals, which can be shown to make an angle of 109° 28' with one another, directed

† L. Pauling, loc. cit.; L. Pauling and J. Sherman, *J. Amer. Chem. Soc.* 1937, 59, 1450.

towards the corners of a regular tetrahedron, the bond strength of these hybrid bonds being in each case equal to 2, which is higher than for a p or s orbital alone. This is also the case for quadrivalent silicon or germanium save that the M ($n = 3$) and N ($n = 4$) valency shells, respectively, are involved in place of the L shell as with carbon. This tetrahedral configuration, and the complete equivalence of the four bonds, corresponds, of course, with the classical structure of compounds of carbon originally postulated by van't Hoff and Le Bel.

s-p-d Hybrid Bonds. Although pure d bonds can have a maximum strength of 2.326 in the relative units given in Table 9, d orbitals alone are seldom used for bond formation. If, however, s and p orbitals are also available for hybridization, it can be shown mathematically that strong $s-p-d$ orbitals, in sets in which the number and directions of the bonds vary according to the combination of orbitals used, can be formed, the maximum possible strength of any $s-p-d$ hybrid bond being 3.

Two important types of $s-p-d$ hybridization occur in connexion with coordination compounds of elements of the transition groups, in which d orbitals are available immediately inside the ordinary valence shell.

The type of bond formed depends, among other things, on the number of these available d orbitals. Thus, in the divalent nickel ion which, compared with the neutral nickel atom, has the electronic constitution

	3d	4s	4p	
Neutral atom: [Ni]	⊙ ⊙ ⊙ ⊙ ⊙	⊙	⊙ ⊙ ⊙	Normal structure
Ni ²⁺ ion: [Ni]	⊙ ⊙ ⊙ ⊙ ⊙	⊙	⊙ ⊙ ⊙	
Ni ²⁺ ion: [Ni]	⊙ ⊙ ⊙ ⊙	⊙	⊙ ⊙ ⊙	
	<div style="border: 1px dashed black; padding: 5px; display: inline-block;"> Coordination orbitals (dsp^2 hybrids) </div>			Structure ii (on occupation of the fifth 3d orbital)

a single 3d orbital (as far as the energetically almost equivalent structure ii is concerned), as well as the single 4s and all the 4p orbitals, are vacant for possible acceptance of electron pairs for the formation of coordination compounds. On mathematical treatment, it can be shown that in such a case a set of four strong hybrid dsp^2 bonds can be formed, all in the same plane and directed towards the corners of a square, the strength of these bonds being 2.69. Similar bonds should also be formed by the Pd²⁺ and Pt²⁺ ions.

If orbitals of this type are actually used, the coordination complex should have a coplanar (square) form. This is known to be the case, for instance, in the $[\text{Ni}(\text{CN})_4]^{2-}$ ion and in nickel compounds of the glyoximes. The coordination number of the nickel is, of course, 4; and the square configuration can be differentiated from the alternative tetrahedral form on the strength of magnetic evidence (see later).

Where two vacant d orbitals are available inside the valency shell hybrids of a different type are formed. Thus, in the cobaltic ion two such ($3d$) orbitals, in addition to the $4s$ orbital (see p. 48) and all three of the $4p$ orbitals, are free for the formation of coordinate bonds by electron acceptance from suitable atomic groups. It will be seen from Fig. 3 that all these six orbitals are of approximately the same energy, whereas higher orbitals ($4d$) of the valency shell have a higher energy content (lower stability) if these higher orbitals are used in bond formation. In such a case it is found that maximum stability corresponds with the formation of six equivalent d^2sp^3 hybrid bonds directed towards the corners of a regular octahedron:

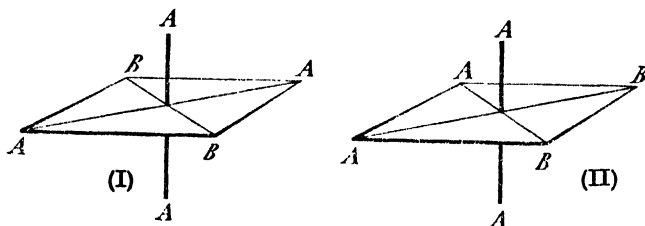


FIG. 9.

This agrees completely with Werner's configuration for coordination compounds of the type $[\text{Co}(\text{R})_6]^{3+}$ —e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$ —and accounts for the observed stereo-isomerism if the coordinated groups are of more than one sort, as is shown by the structures I and II of Fig. 9, in which the groups, B , may either be adjacent or opposite. Similar bonds are also present in the chloroplatinate, ferrocyanide, and ferricyanide ions: $(\text{PtCl}_6)^{2-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and $[\text{Fe}(\text{CN})_6]^{3-}$.

It may be noted, in connexion with all these coordination compounds, that in place of univalent groups such as ammonia or cyanogen bivalent groups such as ethylene diamine, $\begin{array}{c} \text{CH}_2\cdot\text{NH}_2 \\ | \\ \text{CH}_2\cdot\text{NH}_2 \end{array}$, may be coordinated to the central atom. Such groups are known as chelate groups (G. T. Morgan). The two nitrogen atoms of such a donor

molecule can only attach themselves to the same multivalent acceptor atom by occupying neighbouring, i.e. *cis*, positions.

A further type of *s-p-d* hybridization, probably involving *dsp*³ bonds (the *d* in a lower shell), leads to five equivalent bonds directed towards the corners of a trigonal bi-pyramid, as shown in Fig. 8; and bonds of this type are probably responsible for the structure of pentahalides such as PCl₅, PI₅, IF₅, MoCl₅, NbCl₅, and TaCl₅ in the gaseous or liquid state. For the structure of these molecules in the solid form (as a polymolecular crystal lattice) reference should be made to the work of Skinner and Sutton.†

Kimball's Summary of Directed Valency Types

The above and other possible types of directed pure and hybrid bonds have been considered systematically by Kimball,‡ whose classification is summarized in Table 8. The bonds given are all single, i.e. electron-pair, covalent bonds; but various types of strong and weak links possessing some double-bond character also exist, for the nature of which reference should be made to Kimball's paper.

TABLE 8

<i>Covalency</i>	<i>Configuration</i>	<i>Arrangement</i>
2	<i>sp</i> or <i>dp</i>	Linear
	<i>p</i> ² , <i>ds</i> , or <i>d</i> ²	Angular
3	<i>sp</i> ² , <i>dp</i> ² , <i>d</i> ² <i>s</i> , or <i>d</i> ³	Trigonal plane
	<i>dsp</i>	Unsymmetrical plane
	<i>p</i> ³ or <i>d</i> ² <i>p</i>	Trigonal pyramid
4	<i>sp</i> ³ or <i>d</i> ³ <i>s</i>	Tetrahedral
	<i>dsp</i> ² or <i>d</i> ² <i>p</i> ²	Tetragonal plane
	<i>d</i> ² <i>sp</i> , <i>dp</i> ³ , or <i>d</i> ³ <i>p</i>	Irregular tetrahedron
	<i>d</i> ⁴	Tetragonal pyramid
5	<i>dsp</i> ³ or <i>d</i> ³ <i>sp</i>	Bi-pyramid
	<i>d</i> ² <i>sp</i> ² , <i>d</i> ⁴ <i>s</i> , <i>d</i> ² <i>p</i> ³ , or <i>d</i> ⁴ <i>p</i>	Tetragonal pyramid
	<i>d</i> ³ <i>p</i> ²	Pentagonal plane
	<i>d</i> ⁵	Pentagonal pyramid
6	<i>d</i> ² <i>sp</i> ³	Octahedron
	<i>d</i> ⁴ <i>sp</i> or <i>d</i> ⁵ <i>p</i>	Trigonal prism
	<i>d</i> ³ <i>p</i> ³	Trigonal antiprism
8	<i>d</i> ⁴ <i>sp</i> ³	Dodecahedron
	<i>d</i> ⁵ <i>p</i> ³	Antiprism
	<i>d</i> ⁵ <i>sp</i> ³	Face-centred prism

† H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.* 1940, **36**, 668.

‡ G. E. Kimball, *J. Chem. Phys.* 1940, **8**, 194.

RELATIVE BOND STRENGTHS

The relative bond strengths of a given atom for some of the more important types of bonds, as calculated by Pauling, are, for convenience of reference, collected in Table 9.

TABLE 9

<i>Type of bond</i>	<i>Number of bonds in set</i>	<i>Directional character</i>	<i>Relative strength</i>
<i>s</i>	1	Non-directional	1
<i>p</i>	3	Orthogonal	$\sqrt{3}$ (= 1.732)
<i>d</i>	5	See p. 54	2.236
<i>sp³</i>	4	Tetrahedral	2
<i>dsp²</i>	4	Square (coplanar)	2.694
<i>d²sp³</i>	6	Octahedral	2.923

ATOMIC RADII AND INTERATOMIC DISTANCES IN MOLECULES

The principal methods used for the measurement of interatomic distances are:

- (i) The interpretation of X-ray or electron diffraction patterns.
- (ii) The determination of molecular moments of inertia from rotational spectra, and the derivation from these of the distances separating the known atomic masses.

From these distances the valency angles and consequently the shape of simple molecules can be obtained, e.g. if, in a three-atom molecule, B—A—B, the distances B—A and B—B are known, the valency angle BAB can easily be derived.

Where the interatomic distance corresponds with a bond this distance can usually be calculated additively from tables of atomic radii with a fair degree of agreement with the observed value, i.e. if r_a and r_b are the effective atomic radii of two atoms, A and B, the interatomic distance A—B will be approximately $r_a + r_b$. The effective atomic radius of an element varies with the nature of the bond formed. Thus, if a covalent or principally covalent link is involved the effective radius varies with the orbital type and with the multiplicity (single, double, or triple bond); and it will also be affected by the degree of occurrence of any partial ionic character in the bond and by resonance in general. If the link is ionic, as in an ionic crystal, the radius varies with the ionic charge, e.g. the effective radius of Fe^{2+} is not the same as that of Fe^{3+} : further, the ionic radius of an element is in general quite different from its covalent radius.

A list of atomic radii, containing the values adopted by Pauling and Huggins† and by Schomaker and Stevenson,‡ is given in Table V of the Appendix. Covalent radii are more definite than ionic radii; but, even with these, the actual bond lengths often differ somewhat from the length calculated on the basis of the radius sum.

Schomaker and Stevenson have shown that the departure of the observed interatomic distances from the additivity rule can, in the case of a single covalent bond having a partial ionic character, often be expressed fairly satisfactorily by the third term on the right-hand side of the equation

$$r_{ab} = r_a + r_b - 0.09(x_a - x_b),$$

in which $(x_a - x_b)$ is the absolute value of the difference in the Pauling electronegativities of the atoms A and B. The electronegativity of an element is its attraction for electrons when it is in an uncharged state in a molecule.§ Some examples, taken from Schomaker and

TABLE 10
Diatomic Molecules (Hydrogen Halides)

<i>Substance</i>	<i>Percentage ionic character of bond (Pauling)</i>	<i>Observed interatomic distance μ</i>	<i>$r_a + r_b$ (Schomaker and Stevenson)</i>	<i>Interatomic distance (calc.)</i>
HF	50	0.92	1.09	0.92
HCl	17	1.28	1.36	1.28
HBr	11	1.41	1.51	1.45
HI	5	1.60	1.70	1.67

Polyatomic Molecules

<i>Bond</i>	<i>Compound</i>	<i>Interatomic distance (obs.)</i>	<i>$r_a + r_b$</i>	<i>Interatomic distance (calc.)</i>
C—H	CH ₄	1.09	1.14	1.10
Si—H	SiH ₄	1.42	1.54	1.51
N—H	NH ₃	1.01	1.11	1.03
P—H	PH ₃	1.40	1.47	1.47
As—H	AsH ₃	1.54	1.58	1.57
O—H	H ₂ O	0.97	1.11	0.98
S—H	H ₂ S	1.42	1.54	1.51
Se—H	H ₂ Se	1.50	1.54	1.51

† L. Pauling and M. L. Huggins, *Z. Krist.* 1934, **87**, 205.

‡ V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.* 1941, **63**, 37.

§ See Pauling, *Nature of the Chemical Bond*, p. 58.

Stevenson's paper, of the deviation of various diatomic and polyatomic molecules from the additivity rule are given in Table 10, the last column of which gives the interatomic distances calculated by the above equation.

It will be seen that the agreement is very good for the diatomic hydrogen compounds of the lighter halogens (i.e. for HF and HCl, in which the bond has a considerable degree of ionic character) and for the polyatomic hydrides of the first-row elements (CH_4 , NH_3 , and H_2O), but that the proposed equation is far less satisfactory for hydrides of the heavier elements in each series.

MOLECULAR SHAPES

The geometrical form of some typical polyatomic molecules, calculated from the observed interatomic distances, is discussed below. For reasons of space, for molecules containing more than three atoms, the treatment has been limited to compounds of the type AB_n .

Three-Atom Complexes





Complexes of the types A_3 , A_2B (AB_2), or ABC may be linear, angular, or, more rarely, cyclic. With polar linear molecules it is possible to distinguish between a symmetrical structure, B—A—B , and an unsymmetrical structure, A—B—B , not only by determining the interatomic distances but also by measuring the electric dipole moment, since the symmetrical form should have a zero electric moment.

The geometrical structure of and interatomic distances in some inorganic molecules of the three-atom class are given in Table 11. The bonds shown in the structures are not necessarily single ones.

Covalent Molecular Types AB_n (where $n = 3$ to 8)

Data relating to the structure of some representative molecules of the forms AB_3 , AB_4 , AB_5 , AB_6 , AB_7 , and AB_8 are given in Table 12. It will be seen that these shapes correspond closely, for a complex of a given type, with one or other of the possible configurations which can be derived from the wave-mechanical treatment of valency bonds. The experimental evidence for the shape of the last five molecules in the table is less certain than for the remaining compounds; but they have been included for completeness, mainly in order to provide examples of the probable shape of the few known complexes of the types AB_7 and AB_8 .

TABLE 11

<i>Molecule</i>	<i>Structure</i>	<i>Interatomic distances in Å</i>	<i>Shape</i>	<i>Electric dipole moment, in e.s.u. $\times 10^{18}$</i>
CO ₂	O—C—O	C—O = 1.13 ¹ O—O = 2.26	Linear (symm.)	0
CS ₂	S—C—S	C—S = 1.54 ² S—S = 3.08	Linear (symm.)	0
COS	O—C—S	C—O = 1.16 ³ C—S = 1.56	Linear	—
HgCl ₂ (gas)	Cl—Hg—Cl	Hg—Cl = 2.34 ⁴ Cl—Cl = 4.68	Linear (symm.)	0
N ₂ O	N—N—O	O to further N = 2.38 ⁵	Linear (unsymm.)	0.14
HCN	H—C—N	C—N = 1.154 ⁶ C—H = 1.08	Linear	2.6
H ₂ O		O—H = 1.013 ⁷ H—H = 1.53 Angle HOH = 105°	Angular	1.84
H ₂ S		H—S = 1.35 Angle HSH = 92°	Angular	0.93
SO ₂		S—O = 1.37	Angular	1.61
OF ₂		Angle FOF = 100°	Angular	—

¹ L. Gero, G. Herzberg, and R. Schmid, *Phys. Rev.* 1937, **52**, 467.² P. C. Cross and L. O. Brockway, *J. Chem. Phys.* 1935, **3**, 821; R. Wierl, *Ann. Phys.* 1931, **8**, 541. ³ R. W. Dornte, *J. Amer. Chem. Soc.* 1933, **55**, 4126.⁴ A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.* 1937, **33**, 852; H. Braune and S. Knoke, *Z. physikal. Chem.* 1933, B **23**, 163. ⁵ R. Wierl, loc. cit.⁶ G. Herzberg, F. Patat, and J. W. T. Spinks, *Z. Physik*, 1934, **91**, 386; F. Rasetti, *Phys. Rev.* 1929, **34**, 367; H. A. Stuart, *Molekülstruktur*, J. Springer, Berlin, 1934, p. 362.⁷ R. Mecke and W. Baumann, *Physikal. Z.* 1932, **33**, 833; see Stuart, loc. cit., from which some of the other data have also been derived.⁴ H. A. Skinner and L. E. Sutton, *ibid.* 1940, **36**, 681.⁵ L. O. Brockway, *Rev. Mod. Phys.* 1936, **8**, 260.⁶ V. Schomaker. See Pauling, *Chemical Bond*, p. 103.⁷ R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.* 1938, **34**, 1358.⁸ H. A. Skinner and L. E. Sutton, *ibid.* 1940, **36**, 681.⁹ H. Braune and S. Knoke, *Z. physikal. Chem.* 1933, B **21**, 292.¹⁰ G. C. Hampson and L. Pauling, *J. Amer. Chem. Soc.* 1938, **60**, 2702.¹¹ J. L. Hoard and H. H. Nordsieck, *ibid.* 1939, **61**, 2853.

TABLE 12

Co- valency	Molecule	Shape	Bond distance		Bond angle	μ , e.s.u. $\times 10^{18}$
			a. Obs.	b. Calc. by sum- mation of co- valent radii		
3	BF ₃	Trigonal plane	1.31 ¹	1.53	120°	0
	BCl ₃	" "	1.75 ¹	1.88	120°	0
	PCl ₃	Trigonal pyramid	2.00 ²	2.09	100°	1.16
	AsCl ₃	" "	2.16 ²	2.20	100°	2.17
	SbCl ₃	" "	2.37 ³	2.40	100°	3.12
	BiCl ₃	" "	2.48 ⁴	2.50	100°	—
4	(PdCl ₄) ²⁻	Square (planar)	2.29	2.31	90°	—
	(PtCl ₄) ²⁻	" "	2.32	2.31	90°	—
	CCl ₄	Regular tetrahedron	1.755 ⁵	1.76	109°	0
	SiCl ₄	" "	2.00 ²	2.16	109°	0
	SnCl ₄	" "	2.29 ²	2.39	109°	0
5	PF ₅	Trigonal bi-pyramid	1.57 ²	1.74	90° 120° 180°	0
	PCl ₅ (gas)	" "	2.04 and 2.11 ⁶	2.09	—	—
	MoCl ₅	" "	2.27 ⁷	—	—	—
	NbCl ₅	" "	2.29 ⁸	2.39	—	—
	TaCl ₅	" "	2.30 ⁸	2.39	—	—
6	SF ₆	Regular octahedron	1.56 ⁹	1.65	—	—
	SeF ₆	" "	1.67 ⁹	1.78	—	—
	TeF ₆	" "	1.82 ⁹	1.92	—	—
	(PtCl ₆) ²⁻	" "	2.3	2.3	—	—
	UF ₆	Probably rhombic symmetry. ¹	—	—	—	—
7	WF ₆	" "	—	—	—	—
	MoF ₆	" "	—	—	—	—
	(ZrF ₇) ³⁻	Octahedron distorted by insertion of 7th F atom. ¹⁰	—	—	—	—
8	[Mo(CN) ₈] ⁴⁻	Dodecahedron with 8 vertices and tri- angular faces. ¹¹	—	—	—	—

¹ H. Braune and P. Pinnow, *Z. physikal. Chem.* 1937, B 35, 239.² L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.* 1938, 60, 1836; L. O. Brockway and F. T. Wall, *ibid.* 1934, 56, 2373.³ A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.* 1937, 33, 852.

For notes 4-11 see opposite.

For a systematic treatment of molecular shape from the standpoint of the electronic theory of valency, reference should be made to a lecture by Sidgwick and Powell.†

VALENCE-BOND RESONANCE (BOND-MULTIPLICITY HYBRIDISM)

In earlier sections (pp. 50–61) consideration has been given to two types of resonance, namely, firstly, to the effect of electron-exchange resonance in general in the formation of *all* covalent bonds and, secondly, to the special type of further stabilization (orbital hybridization) which may occur in certain cases in which there is an appreciable probability of the participation of orbitals of different orders (*s*, *p*, *d*, etc.) from a given atom in the formation of a bond.

In addition, a bond may have a hybrid structure from the standpoint of its multiplicity: for instance, it may be neither a pure single nor a pure double (or higher) bond, but a resonance hybrid in the formation of which bonds of differing multiplicities are involved as components. Such a bond will, of course, be stabilized by the resonance energy, as has already been discussed.

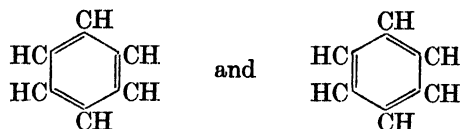
It is convenient to regard this type of hybridism as involving resonance between alternative molecular structures having different electronic configurations. Molecules in which such resonance occurs are characterized by abnormal stability, which is shown by an unexpectedly high value for their heat of formation, the difference between the measured and the expected heats representing the resonance energy; and the resonance will also in general affect the bond length. This existence of molecules in a state which cannot be adequately represented by any one valence-bond formula is sometimes called mesomerism. It must be sharply differentiated from tautomerism, which merely denotes an equilibrium (not a hybridization) among molecules of alternative structures.

Valence-bond resonance is a very common and widely distributed effect. It can probably be most simply illustrated by considering the case of benzene, although this is an organic rather than an inorganic molecule. If the experimentally measured heat of formation of benzene is compared with the value which can be calculated on the basis of alternate single and double bonds, it is found that the observed heat is higher, by 39 kg.-cals. per mole, i.e. the benzene molecule is

† N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc.* 1940, A 176, 153 (Bakerian Lecture).

more stable, by this energy value, than would be expected from the Kekulé formula. Further, the carbon-carbon bond lengths in benzene are found, on measurement, to have a *uniform* value of 1.39 Å. They thus cannot consist of alternate single and double bonds, which would involve alternate bond lengths of 1.54 and 1.33 Å. The absence of ordinary double bonds is also borne out by chemical evidence.

This stabilization, and the uniform and special nature of the bonds, can be explained simply if the normal state of benzene is viewed as a hybrid structure towards which the structures



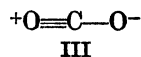
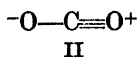
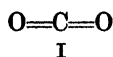
contribute approximately equally, with subordinate contributions from other excited structures.

The oxides of carbon provide simple examples of the same type of hybridism in what are more nearly inorganic molecules. Thus, if the heat of formation and the carbon-oxygen bond length in carbon dioxide are calculated for the conventional structure, $\text{O}=\text{C}=\text{O}$, on the basis of the normal carbon-oxygen double bond as in, for instance, a ketone, it is found that considerable discrepancies exist between the observed and the calculated figures. These are

	Calculated	Observed
Heat of formation (kg.-cals.) . . .	348	380
Carbon-oxygen bond length (Å) . . .	1.24	1.15†

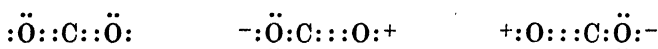
Each of these differences is outside the experimental error. It is known, further, that there is only one uniform (not two different) carbon-oxygen interatomic distance, which in itself renders impossible the actual physical existence of unsymmetrical alternative structures such as $\text{O}-\text{C}\equiv\text{O}$.

The whole question becomes simplified if viewed from the standpoint of resonance, according to which the carbon-oxygen bonds in carbon dioxide are identical but of a hybrid nature, towards which double-, single-, and triple-bond character all contribute, the carbon dioxide molecule being regarded as resonating among the alternative structures:



† W. V. Houston and C. M. Lewis, *Phys. Rev.* 1931, **38**, 1872.

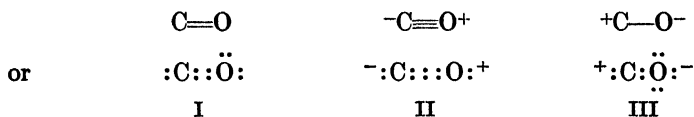
or, written electronically:



If the electrons assigned conventionally to the oxygen atoms in the unsymmetrical single-triple-bond forms are counted, it will be seen that these forms are polar, as marked.

It should again be emphasized that none of these structures, by itself, has an actual physical existence in the normal molecule. The additional stability gained by resonance is represented by the energy difference of 32 kg.-cals. between the actual and the calculated heats of formation. In this instance, the calculated energy of formation is approximately the same for all three structures, since the total energy of four carbon-oxygen bonds is not affected greatly by their distribution into two double bonds or into one single and one triple bond. The contribution of the various structures to the normal structure can readily be calculated;† and it can be shown that, in the normal dioxide molecule, all three structures contribute approximately equally.

The case of carbon monoxide is very similar. Its measured heat of formation is about 60 kg.-cals. in excess of that calculated for a normal C=O ketonic bond; and the bond length‡ is about 1.13 Å, compared with a calculated distance of 1.15 Å (the sum of the normal covalent radii, 0.67 and 0.57 Å, for doubly linked carbon and oxygen, less a correction of 0.09 Å for the incomplete valency shell effect). It will be seen that here the chief discrepancy lies in the increased stability. Carbon monoxide is regarded as resonating among the three structures given below, with more or less equal contributions from each.



The approximately equal contribution of structures II and III is shown by the very low value of the electric dipole moment.

In addition to the above molecules, very many other inorganic molecules show signs of bond-multiplicity hybridism both by reason of unexpected stability and by the (often more easily detectable) presence of abnormal bond lengths. Such hybrid bonds occur, for

† For the method of calculation see Pauling, *Nature of the Chemical Bond*, p. 82.

‡ L. Gerö, G. Herzberg, and R. Schmid, *Phys. Rev.* 1937, **52**, 467.

instance, in many of the simple oxy-acid ions, in the covalent oxy-halides and in many other molecules involving oxygen or sulphur. Thus the sulphur-oxygen links in the sulphate ion, in which the S—O bond length is 1.51 Å in place of the radius-sum value of 1.70, are probably resonance hybrids formed principally by contributions from single- and double-bond components; and the same type of hybridism seems also to exist in the S—O bond of SO₂.

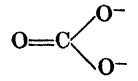
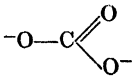
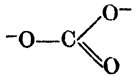
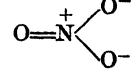
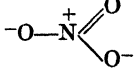
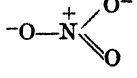
The existence of some degree of double-bond character in a number of principally single bonds has recently been reviewed by Sutton,† from whose summary the examples given in Table 13 are taken.

TABLE 13

Bond	Compound	Bond length in Å (obs.)	Bond length (calc.)		
			Single	Double	Triple
SO	SO ₂	1.43	1.70	1.52	1.47
	SO ₂ Cl ₂	1.43	1.70	1.52	1.47
PO	POF ₃	1.55	1.76	1.57	1.44
PS	PSF ₃	1.85	2.14	1.95	1.81

Some other examples of resonance in inorganic molecules are given in Table 14.

TABLE 14

Molecule	Resonance components				Resonance energy in kg.-cals. per mole
CS ₂	S=C=S	-S—C≡S ⁺	and	+S≡C—S ⁻	11
COS	S=C=O	-S—C≡O ⁺	and	+S≡C—O ⁻	20
N ₂ O	-N ⁺ =N=O and N≡N ⁺ -O ⁻				
(CO ₃)			and		42
(NO ₃)			and		45

MAGNETIC EVIDENCE FOR MOLECULAR STRUCTURE

It is in many cases possible, as has been pointed out by Pauling and others,‡ to apply magnetic criteria for the determination of

† L. E. Sutton, *Ann. Reports Chem. Soc.* 1940, **37**, 75.

‡ L. Pauling, *J. Amer. Chem. Soc.* 1931, **53**, 1391; S. Sugden, *J. Chem. Soc.* 1932, 161; E. Rosenbohm, *Z. physikal. Chem.* 1919, **93**, 693.

molecular structure, including the type of bonding in coordination and other compounds, the method being based on the principle that a spinning electron acts as a small magnet.

In general, while all atoms possess inherent diamagnetic properties leading to a relatively weak repulsion by a magnet, far stronger magnetic properties of opposite sign (paramagnetism, associated with attraction by a magnet) may be developed partly by virtue of the spin of unpaired electrons and partly by reason of their orbital motion. Paired electrons lead to a zero moment, since the spins neutralize one another.

If S is the total spin number of the electrons in an electronic subgroup containing unpaired electrons (where $S = \sum s$ and $s = \frac{1}{2}$ for each unpaired electron) and L is their orbital magnetic moment, the paramagnetic magnetic moment, μ , in Bohr magnetons, due to the electronic group, will be:

$$\mu = \sqrt{4S(S+1)} \quad (i)$$

if only the contribution of the electronic spins is taken into account,

or
$$\mu = \sqrt{4S(S+1) + L(L+1)} \quad (ii)$$

if the orbital moment is also considered.

In the case of molecules containing atoms of elements in or near the transition groups, it is found, particularly in condensed systems, that the actual magnetic moment, as measured experimentally, is almost entirely determined by the unpaired spin factor (equation (i)). This is ascribed by Pauling to the perturbing effect of atoms or molecules surrounding a magnetic atom, as a result of which the contribution of the orbital momentum to the magnetic moment is quenched, and the resultant magnetic moment of the atom is due entirely to the spin moments of the unpaired electrons.

The calculated values of μ on the basis of spin alone are as follows:

TABLE 15

<i>Number of unpaired electrons</i>	μ_s
0	0
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92
6	6.93

and the agreement of these values with observed moments may be illustrated by the magnetic moments of manganese ions of various valencies.† As will be seen from the electronic diagram:

	3d					4s	
[Mn]	○	○	○	○	○	○	Neutral Mn
[Mn]	○	○	○	○	○	○	Mn ²⁺
[Mn]	○	○	○	○	○	○	Mn ³⁺
[Mn]	○	○	○	○	○	○	Mn ⁶⁺
[Mn]	○	○	○	○	○	○	Mn ⁷⁺

the number of unpaired electrons in the various ions is as given in Table 16.

TABLE 16

	Number of unpaired electrons	Magnetic moment, calculated	μ , observed
Mn ²⁺	5	5.92	5.92 (MnCl ₂); 5.93 (MnSO ₄)
Mn ³⁺	4	4.90	5.04 (MnPO ₄); 5.19 (Mn ₂ (SO ₄) ₃); 5.08 (MnCl ₃)
Mn ⁶⁺	1	1.73	1.69–1.73 (K ₂ MnO ₄)
Mn ⁷⁺	0	0	0 (KMnO ₄)

The agreement between the observed and the calculated values of μ is shown in the last two columns of the table.

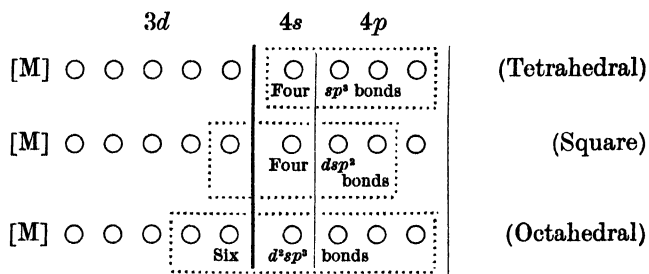
In the case of coordination compounds, the number of electrons remaining unpaired will depend on the number and distribution of the coordinate links, namely, on the number and nature of the orbitals used for bonding and on any consequent rearrangement of electrons. Pauling gives the following generalizations, which permit the number of unpaired electrons to be estimated (having regard to the coordination number shown by the central coordinating atom) for various types of bonding:

1. Bond orbitals for atoms of the iron group are formed from the nine orbitals: five 3d, one 4s, and three 4p. One bond orbital is required for each electron pair accepted.
2. The remaining (unshared) electrons tend to occupy as far as possible 3d orbitals not involved in bond formation, i.e. the 4s and 4p orbitals fill up first, and the 3d electrons remain unpaired until forced to pair by crowding.
3. The normal state is the state with the maximum resultant spin, S , allowed by the Pauli principle.

† N. Goldenberg, *Trans. Faraday Soc.* 1940, **36**, 847.

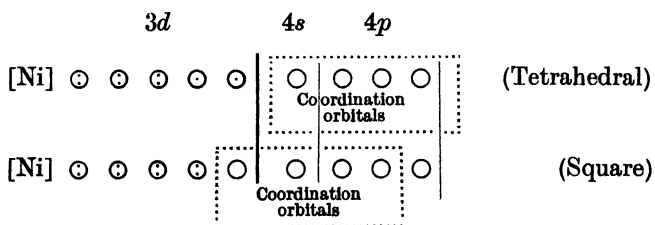
Similar rules, with appropriate changes in the principal quantum numbers, apply to the palladium and platinum groups of elements.

The effect of various types of bonding (four tetrahedral sp^3 bonds, four coplanar dsp^2 bonds, or six octahedral d^2sp^3 bonds) on the number of remaining $3d$ orbitals—which contain any unpaired electrons—is shown below; and, for any particular case, the remaining electrons must be fitted into the unused d orbitals according to the above rules. Coordination compounds involving eight electron-pair bonds also occur but are less common.



It will be seen that the tetrahedral, sp^3 , type of bonding leaves the d orbitals unaffected: accordingly the magnetic moment will be the same as for the uncoordinated ion. The square (dsp^2) bonding, on the other hand, uses one d orbital; and the value of the magnetic moment can thus be used to differentiate between coplanar and tetrahedral bonding.

A well-known instance of this is the assignment of a square configuration to many nickel compounds of coordination number 4. Thus, for the $[\text{Ni}(\text{CN})_4]^{2-}$ ion, the following bondings, apart from ionic linking, are possible:



On the basis of the square form, the ion, in that it has no unpaired electrons, should have zero magnetic moment, whereas a tetrahedral grouping would give a moment of 2.83. Actual measurements have shown a zero moment (in fact, $[\text{Ni}(\text{CN})_4]^{2-}$ is slightly diamagnetic),

the square configuration being thus confirmed. Similar evidence has also been obtained for nickel dimethyl- and diphenyl-glyoxime, as well as for many other coordination compounds of divalent nickel containing four coordinated groups; but paramagnetic compounds of nickel also exist with μ of the order of 3, in addition to others which, on the strength of magnetic evidence are of less definite bond types.

Some indication of the degree to which magnetic criteria can be used to differentiate between the various types of bonding in covalent coordination compounds of the transition series can be obtained from Table 17, which is due to Pauling.[†]

TABLE 17

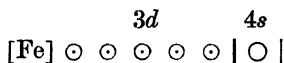
Ion			Calculated values of μ_s for		
			Uncoordinated ion or four sp^3 bonds	Four d^2sp^3 bonds	Six d^2sp^3 bonds
Fe^{4+}	Ru^{4+}	Os^{4+}	4.90	4.90	2.83
$\text{Fe}^{3+}, \text{Co}^{4+}$	Ru^{3+}	$\text{Os}^{3+}, \text{Ir}^{4+}$	5.91	3.88	1.73
$\text{Fe}^{2+}, \text{Co}^{3+}$	$\text{Ru}^{2+}, \text{Rh}^{3+}, \text{Pd}^{4+}$	$\text{Ir}^{3+}, \text{Pt}^{4+}$	4.90	2.83	0.00
$\text{Co}^{2+}, \text{Ni}^{3+}$	Rh^{2+}	—	3.88	1.73	—
Ni^{2+}	$\text{Rh}^{+}, \text{Pd}^{2+}$	Pt^{2+}	2.83	0.00	—

As further examples, $(\text{PtCl}_4)^{2-}$ in K_2PtCl_6 and $[\text{Pt}(\text{C}_2\text{O}_4)]^{2-}$ in potassium platino-oxalate, on the basis of their observed zero magnetic moment, have a coplanar (square) configuration like nickel in $[\text{Ni}(\text{CN})_4]^{2-}$.

With ions having a coordination number of 6, the bonds involved, if covalent, must be octahedral d^2sp^3 bonds; but the bonding may—as is, of course, the case in all coordination compounds—be of the ionic type, it being usually possible to differentiate between the alternative covalent and ionic structures by means of the value of μ . Thus, K_2PtCl_6 (which is formed from the Pt^{4+} ion) and potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$ (derived from the Fe^{2+} ion) both have zero magnetic moment corresponding with six d^2sp^3 links. In the case of the ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, a six d^2sp^3 bond condition would, as will be seen from the table, require a magnetic moment of 1.73 since the complex is based on a Fe^{3+} ion. The observed value of μ is about 2,

[†] L. Pauling, *J. Amer. Chem. Soc.* 1931, loc. cit.

which agrees substantially with that expected. On the other hand, moments agreeing with ionic linkages are obtained for a number of other coordination compounds of elements of the transition series, particularly if the element is coordinated with water or with fluorine. Thus, the fluorine in the $(\text{FeF}_6)^{3-}$ ion—in $(\text{NH}_4)_3\text{FeF}_6$ which is formed from the Fe^{3+} ion—is, as has been pointed out by Pauling, linked ionically, the complex ion FeF_6 containing the original ferric ion:



with five unpaired electrons and having both calculated and observed values of 5.9 for the magnetic moment. The presence of ionic linkages can, of course, also be detected chemically in many cases on the basis of dissociation or participation in ionic reactions.

FREE RADICALS

Free radicals are complexes which, in spite of the possession of active free valencies which give them additive properties, have a life sufficiently long for their detection or even, in the case of specially long-lived radicals, for their isolation and study in the ordinary way.

The earliest known class of free radicals is represented by triphenylmethyl, $(\text{C}_6\text{H}_5)_3\text{C}$ —, which was made by Gomberg† in 1900 by acting on triphenylchloromethane, $(\text{C}_6\text{H}_5)_3\text{CCl}$, with finely divided silver. This radical has a long life and can accordingly be analysed and examined without difficulty. On the other hand, the presence of short-lived radicals, such as free methyl or ethyl (which are formed during the decomposition of lead tetra-methyl or tetra-ethyl,‡ or by the action of sodium vapour on the vapour of the alkyl iodide§), has usually to be inferred by their additive properties in a streaming gas, e.g. by the direct formation of an alkyl halide by the addition of a halogen, or by their absorption band spectrum.

A considerable amount of work has now been done on the production of free inorganic radicals (OH , SO , SO_4 , etc.) in discharge tubes, by various radiation methods and by the chemical abstraction of an element from a stable molecule. Some of this work will be described in Chapter VI. In addition, claims have been made for the prepara-

† M. Gomberg, *J. Amer. Chem. Soc.* 1900, **22**, 757; *Ber.* 1900, **33**, 3150.

‡ F. Paneth and W. Hofeditz, *ibid.* 1929, **62**, 1355; F. Paneth and W. Lautsch, *ibid.* 1931, **64**, 2702.

§ E. Horn, M. Polanyi, and D. W. G. Style, *Trans. Faraday Soc.* 1934, **30**, 189.

tion of long-lived inorganic free radicals: thus, Gomberg (see p. 136) has put forward evidence for the formation of ClO_4 by the action of halogens on silver perchlorate in ether solution.

Some general considerations relative to free radicals may be dealt with briefly. A free radical may be regarded as a structure, the electron system of which possesses an unbalanced spin moment and is thus easily able to form an additive coupling with neighbouring molecules. As has been pointed out by Mecke,[†] this conception of a free radical leads to the possibility of the existence of one and the same molecule either as a stable compound or as an unstable radical by reason of a regrouping of its electrons. Thus, nitrogen or carbon monoxide, which are normally inert, pass, on excitation by sufficient energy (about 140 kg.-cals. per mole in each case), into very reactive radicals, $-\text{N}=\text{N}-$ and $=\text{C}=\text{O}$, the existence of which in the free state has been detected spectroscopically and which, when in combination as the azo and carbonyl groups respectively, play an important part in organic chemistry.

By virtue of their unbalanced electronic spin such free radicals are paramagnetic; and their concentration can accordingly often be conveniently estimated magnetically (see, for instance, the $\text{ClO}_3 \rightleftharpoons \text{Cl}_2\text{O}_6$ equilibrium, discussed on p. 135). In this connexion the case of oxygen may be mentioned. Mulliken[‡] has found, on the basis of spectroscopic evidence, a $^3\Sigma$ ground term for the oxygen molecule, two electrons remaining unpaired and giving rise to the paramagnetism of the molecule in spite of its even-electron structure. From this standpoint, oxygen (also NO , NO_2 and other molecules) has some similarity to free radicals; and the inactivity of the oxygen molecule for additions, in spite of its structure, is of considerable interest. Even with typical free radicals, an odd-electron structure is by no means an essential characteristic: thus the $=\text{CH}_2$ radical, which is a commonly occurring molecular species in positive ray analysis, contains an even number of valency electrons.

MOLECULAR ROTATION AND VIBRATION

In addition to any capacity which a molecule may have for free translation, it possesses degrees of freedom associated with rotation and with interatomic vibration.

[†] R. Mecke, *Trans. Faraday Soc.* 1934, **30**, 200.

[‡] R. S. Mulliken, *Phys. Rev.* 1928, **32**, 880.

General Rotation

In the first place, a free molecule may rotate as a whole about its centre of gravity. It is convenient mathematically to regard this general rotation as being resolvable into three component rotations executed about rectangular coordinates having the centre of gravity of the molecule as the origin; although, in the case of a diatomic or other linear molecule, the treatment of its general rotation can be simplified by resolving this rotation into two components only,

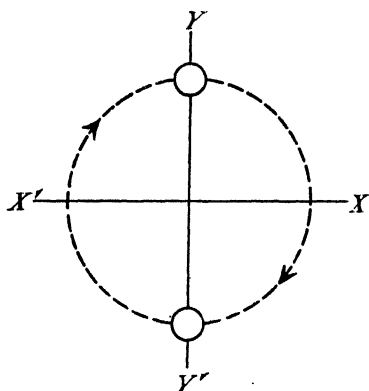


FIG. 10.

namely, along axes perpendicular to the line joining the nuclei, any rotation about the internuclear axis being treated as a spin executed—in a similar rotational sense, if the molecule is rotating as a whole—by the two nuclei. In this connexion it may be noted that it is usual to reserve the term 'rotation' for the rotatory motion of aggregates consisting of more than one atom (molecules and substantial parts of molecules, the geometrical structure of which is usually known) and to designate as

'spin' the similar motion of the still smaller mass units (atomic nuclei, electrons, and other sub-atomic particles) which still have to be treated mathematically as homogeneous spheres.

The general rotation of a diatomic molecule containing, as the simplest case, two nuclei of equal mass, is illustrated in Fig. 10. One of the two resolutes will be in the plane of the paper, as indicated by the dotted line, and the other at right angles to this. The moment of inertia, which can in all cases be calculated for each resolute from the known atomic masses and interatomic distances, will, in this simplest case, be the same for the two resolved rotations.

Internal Rotation

In addition to the general rotation of a molecule as a whole, free internal rotation (or restricted rotation, i.e. oscillation) of a part of a molecule with respect to the remainder may occur about a single bond; but free internal rotation is not possible about a multiple

covalent link. It is convenient to illustrate internal rotation by a molecule of the ethane type (see Fig. 11, in which one of the general rotation components is also indicated); but it, of course, also occurs in inorganic molecules. At low temperatures, at which the internal

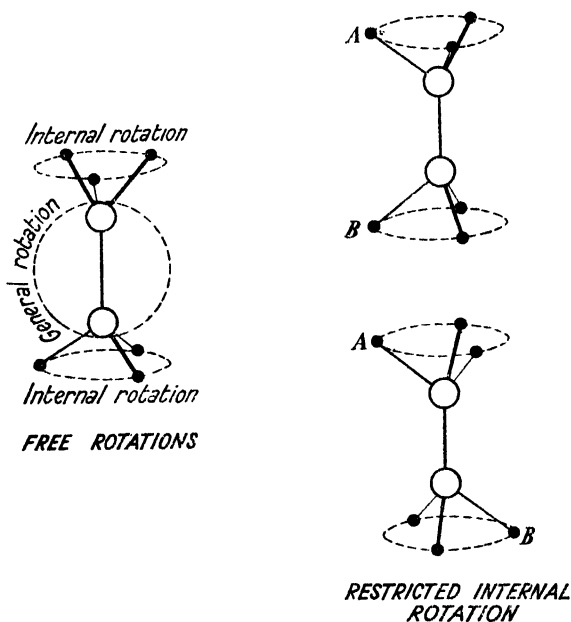


FIG. 11.

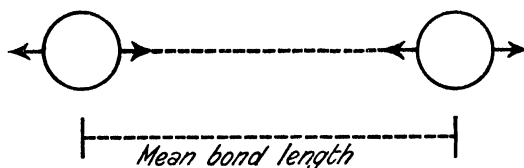


FIG. 12.

rotational energy is low, the internal motion of the two groups about the bond axis will be an oscillation rather than a free continuous rotation: further, the transition of this oscillation into free rotation, as the temperature is increased, will be impeded, or even prevented altogether, if there is appreciable interaction between atoms in the two oscillating groups, as shown on the right of the figure, in which *A* and *B* are bonding or anti-bonding (i.e. repelling) atoms or sub-groups.

Interatomic Vibration

As with general rotation, the nature of the interatomic vibration is simplest for a diatomic molecule, the atoms of which execute vibrational movements, along the bond axis connecting them, about a mean position on this axis as shown in Fig. 12, their mean distance of separation being the mean bond length. With more complicated molecules the number of possible modes of vibration will increase with the number of interatomic bonds present.

QUANTIZATION OF THE VARIOUS FORMS OF INTERNAL ENERGY

The energy inherent in a molecule by virtue of rotational and vibrational movements—in addition to energy associated with the attainment of the various electronic and nuclear energy levels—constitutes the so-called internal energy of the molecule. All these forms of energy are quantized, that is to say, changes in any of these energy forms can only take place in definite quantum jumps; but the order of magnitude of the quanta involved varies greatly with the energy form. Further, the various forms—by virtue of energy partition—are interdependent, so that any change in an energy form requiring a relatively large quantum for a change in level is, in general, also accompanied by subsidiary changes (which may be positive or negative) in the levels of the energy forms requiring smaller quanta for a change in level.

The evidence for the existence of all the above types of energy levels is largely derived from the analysis of absorption or emission spectra, in that a quantum jump is accompanied by the absorption or emission of radiation of frequency $\nu = E/h$. The spectra of free atoms are linear, i.e. consist of sharp lines of definite frequency, and are simpler than those of molecules, which—by virtue of the complicated energy partition among vibrational and rotational levels, in which the quanta involved are very small—have the form of bands, the ultimate linear fine-structure of which is only evident after far greater resolution. The order of magnitude of the energy quanta involved in transitions from level to level in each of the above forms of internal energy is shown in Table 18, the classification being that given by Bowen.†

The size of the quanta involved in changes in a particular energy form represents the relative ease with which a level in the type in

† E. J. Bowen, *The Chemical Aspects of Light*, Clarendon Press, Oxford, 1942, p. 4.

TABLE 18

<i>Nature of energy</i>	<i>Order of magnitude of quanta involved in changes of level within the given energy form</i>		<i>Nature of radiation absorbed or emitted</i>
	<i>a. In ergs per single molecule</i>	<i>b. In kg.-cals. per gram molecule</i>	
Molecular rotation . . .	10^{-14} to 10^{-13}	0.1 to 1	Far infra-red
Vibration of atoms . . .	10^{-13} to 10^{-12}	1 to 10	Near infra-red
Levels in outer electron shells	10^{-11}	100	Visible or ultra-violet
Levels in inner electron shells	10^{-10} to 10^{-8}	10^3 to 10^5	X-rays
Nuclear energy levels .	10^{-7} to 10^{-6}	10^6 to 10^7	γ -rays

question can be affected by external treatment. Thus rotational and vibrational levels are relatively easily changed either by heating or by even low-energy radiation. Electronic levels need somewhat more energetic treatment for their change; and, since the quanta needed for changes in intranuclear levels are very large and are thus only contained in extremely short-wave radiation (see Table 1), only γ -rays are sufficiently active to affect nuclear levels, apart from the alternative method of adding large amounts of energy to a nucleus—either directly or by mass-energy transformation—by means of particulate bombardment.

II

HYDROGEN AND ITS ISOTOPES

THREE isotopes of hydrogen exist, their relative abundance being as given below. ^1H , considered apart from its isotopes, is sometimes known as protium, the term hydrogen being restricted to the ordinary isotopic mixture; but this usage is not common. The isotope ^3H is β -radioactive.

TABLE 19

<i>Isotope</i>	<i>Mass</i>	<i>Symbol</i>	<i>Percentage abundance</i>
Hydrogen . .	1	^1H	99.8
Deuterium . .	2	^2H or D	0.02
Tritium . .	3	^3H or T	$< 10^{-7}$

Before dealing specially with the rarer isotopes, the discovery of which is of recent date, it will be convenient to discuss briefly some of the forms of ordinary hydrogen.

ATOMIC HYDROGEN

a. Preparation by High-Temperature Dissociation

The dissociation of hydrogen at high temperatures was studied in 1925 by Langmuir,† who, on the basis of a value of -98 kg.-cals. for the molecular heat of dissociation of H_2 to 2H , calculated the following figures for the percentage dissociation into atoms at various temperatures.

TABLE 20

<i>Temperature, ° Abs.</i>	<i>Dissociation, per cent.</i>
1,000	3.71×10^{-7}
2,000	0.122
3,000	9.03
4,000	62.3
5,000	94.2

Langmuir found that the recombination, at lower temperatures, of atomic hydrogen produced by blowing the gas through an arc of high current density (for instance, by an arc consuming 20 amps. at 300–800 volts), was accelerated and localized by contact with metals such as tungsten, molybdenum, or tantalum, also by certain oxides, such as thoria, the target being in each case brought to incandescence

† I. Langmuir, *Science*, 1925, **62**, 463; *Gen. Elec. Review*, 1926, **29**, 153.

and finally melted by the heat of recombination. This effect (flames of atomic hydrogen) has been used industrially for welding and other purposes.†

b. Production in Discharge Tubes

Wood‡ showed that if a stream of hydrogen at a low pressure is first exposed to a high-tension discharge and subsequently brought

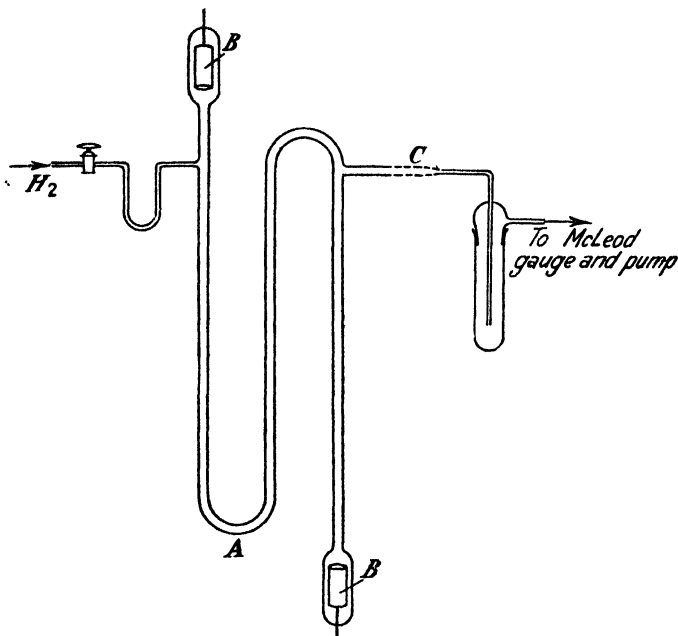


FIG. 13.

into contact with a fragment of tungsten the metal is raised to incandescence by the heat of recombination, as with atomic hydrogen produced by Langmuir's high-temperature method. The gas stream, after passing the discharge tube, was examined spectroscopically by Bonhoeffer,§ who found lines due to atomic hydrogen. It may be noted that somewhat similar experiments to these had been carried out previously by Wendt and Landauer,|| who assumed, however, the production of triatomic hydrogen, H_3 , analogous to ozone.

Bonhoeffer's apparatus is illustrated in Fig. 13. It consisted of

† Brit Pat. 237,898.

‡ R. W. Wood, *Proc. Roy. Soc.* 1923, A 102, 1.

§ K. F. Bonhoeffer, *Z. physikal. Chem.* 1924, 113, 199.

|| G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.* 1920, 42, 930; 1922, 44, 510.

a flexed glass discharge tube, *A*, about 2 cm. in diameter and 2 metres in length, containing two cylindrical electrodes, *B*, of sheet aluminium. Hydrogen was admitted slowly through the tap shown at the left of the figure, a low pressure being maintained by means of the pump. The action of the atomic hydrogen on various substances could be studied by placing them in the gas current at *C*. Von Wartenberg and Schulze† recommend coating the inside of the discharge tube with glacial phosphoric acid in order to minimize the recombining action of the walls.

The formation of atomic hydrogen is facilitated by the presence of water vapour or oxygen: indeed, Urey and Lavin‡ have shown that water vapour itself dissociates in a discharge tube with production of atomic hydrogen. In this case a further constituent of the gas is the free hydroxyl radical (see Chapter VI).

c. Photochemical Formation

Hydrogen may be activated photochemically to give a gas possessing the active properties of atomic hydrogen. Thus,§ if hydrogen containing mercury vapour is illuminated at room temperature by a cooled mercury vapour arc the energy of the resonance radiation ($\lambda = 2537.6 \text{ \AA}$) absorbed by the mercury vapour in the reaction tube is transferred to the hydrogen molecules, dissociating these and giving a gas which is sufficiently active to reduce copper oxide or to hydrogenate ethylene. In order to transfer the radiation energy effectively the mercury vapour discharge tube must be kept cool, otherwise the radiation required is absorbed in the discharge tube itself and does not reach the reaction vessel. In Taylor and Marshall's work, a horizontal quartz mercury arc tube and a horizontal reaction tube (containing hydrogen and, for instance, ethylene, together with a little mercury) were immersed side by side in a water-bath maintained at 15° . The hydrogenation to ethane was complete after about 14 hours exposure.

Properties of Atomic Hydrogen

The duration of the atomic state, although in any case short, is, in the absence of catalysts, longer than would be expected from

† H. v. Wartenberg and G. Schulze, *Z. physikal. Chem.* 1929, B 6, 261.

‡ H. C. Urey and G. I. Lavin, *J. Amer. Chem. Soc.* 1929, 51, 3290.

§ G. Cario and J. Franck, *Z. Physik*, 1922, 11, 162; H. S. Taylor and A. L. Marshall, *J. Phys. Chem.* 1925, 29, 1140.

considerations of simple collision: thus Bonhoeffer estimated a half-lifetime of about 0.3 sec. under the conditions obtaining in the gas stream leaving his discharge tube. A lifetime of this order is, however, compatible with the dependence of recombination on the occurrence of a three-body collision in which the third atom or molecule takes a portion of the high energy of recombination, which, if confined to the resulting H_2 molecule alone would tend to lead to an energetic state sufficiently high to render this unstable and thus to hinder the recombination. It may be noted that more recent figures† for the heat of recombination, determined both thermochemically and on the basis of spectroscopic evidence, give a value of 100 to 105 kg.-cals. per mole. This is a little higher than the figure (98 kg.-cals.) used by Langmuir in his calculation of the $H_2 \rightleftharpoons 2H$ equilibrium.

Hydrogen in the atomic condition is, as would be expected, a very active gas; and, in addition to its rapid recombination when brought into contact with hydrogen-activating catalysts such as platinum, palladium, or the catalysts already mentioned, luminescence results when it is mixed with suitable substances in vapour form: for instance, the vapour of sodium or of the other alkali metals or mercury or anthracene‡ gives characteristic glows when brought into an activated hydrogen current. Zinc phosphors also become luminescent.

Atomic hydrogen is an energetic reducing agent. Bonhoeffer§ found that it reduced copper, lead, bismuth, silver, and mercury oxides or chlorides to metal at room temperature. The sulphides of cadmium, copper, and mercury were also reduced. It may be noted that, whereas Bonhoeffer obtained a negative result for the reduction of nickel or cobalt chloride, these were successfully reduced by Urey and Lavin with atomic hydrogen made by the action of a discharge in water vapour in place of in hydrogen. Even salts of the alkali metals are reduced to the free metal if the anions are of a suitable nature,|| alkali nitrates, nitrites, amides, azides, cyanides, and thiocyanates being reduced while the sulphates, halides, and phosphates are unaffected. Phosphorus pentoxide is, however, reduced to phosphine.

† R. T. Birge (*Proc. Nat. Acad. Sci.* 1928, **14**, 12) gives the value 101.9 kg.-cals. for the heat of dissociation at absolute zero.

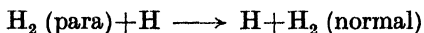
‡ K. F. Bonhoeffer, *Z. physikal. Chem.* 1925, **116**, 391.

§ K. F. Bonhoeffer, *ibid.* 1924, **113**, 199.

|| H. Kroepelin and E. Vogel, *Z. anorg. Chem.* 1936, **229**, 1.

Atomic hydrogen also possesses the additive and milder reducing properties associated with nascent hydrogen or, in a greater degree, with hydrogen in the presence of a catalyst: thus, as already mentioned, ethylene is hydrogenated to ethane, and oleic acid to stearic acid. The reduction of azoxybenzene to azobenzene, hydrazobenzene, and, finally, to aniline, has also been observed.†

Atomic hydrogen causes the normalization of para-orthohydrogen mixtures,‡ in which reaction it apparently acts catalytically:



in a manner similar to the process postulated by Farkas§ for the thermal normalization, in which latter case the hydrogen atoms are produced thermally. The para-ortho conversion thus constitutes a sensitive test for atomic hydrogen.

With suitable free elements hydrides are produced. The hydrides of sodium, potassium, or lithium are formed directly by passing the active gas over these metals at room temperature,|| the reaction being accompanied by the evolution of heat. These hydrides appear to be identical with those formed with ordinary hydrogen at higher temperatures. Sulphur, phosphorus, arsenic, and antimony give hydrogen sulphide, phosphine, arsine, and stibine,¶ and bismuth also gives the hydride. The formation of a hydride of mercury has been reported by Geib and Harteck.††

With oxygen, hydrogen peroxide results, often in high concentration. For instance, in an experiment of Boehm and Bonhoeffer,‡‡ out of 100 c.c. of oxygen admitted in the course of ten minutes, 45 c.c. reacted to form the peroxide. It may be noted that the production of hydrogen peroxide from hydrogen containing a little oxygen and exposed to a glow discharge was studied by Franz Fischer and M. Wolf§§ as long ago as in 1911. Geib and Harteck claim that the peroxide formed by the action of active hydrogen on oxygen at low temperatures differs from the ordinary peroxide but passes into this at -115° with partial decomposition.

† H. C. Urey and G. I. Lavin, *J. Amer. Chem. Soc.* 1929, **51**, 3286.

‡ K. H. Geib and P. Harteck, *Z. physikal. Chem.* 1931, Bodensteinfestband, 849.

§ A. Farkas, *ibid.* 1930, B **10**, 419.

|| E. Ferrell, T. G. Pearson, and P. L. Robinson, *J. Chem. Soc.* 1934, 7.

¶ K. F. Bonhoeffer, *loc. cit.*; T. G. Pearson, P. L. Robinson, and E. M. Stoddart, *Proc. Roy. Soc.* 1933, A **142**, 275.

†† K. H. Geib and P. Harteck, *Ber.* 1932, **65**, 1551.

‡‡ E. Boehm and K. Bonhoeffer, *Z. physikal. Chem.* 1926, **119**, 385.

§§ *Ber.* 1911, **44**, 2956.

SPIN ISOMERS OF MOLECULAR HYDROGEN

(Para- and Orthohydrogen, Para- and Orthodeuterium)

The possibility of the existence of two types of hydrogen molecules, distinguished by the similarity or dissimilarity in the sense of the spin of the two coupled nuclei which make up the molecule, and restricted respectively to odd and to even quantum levels, was predicted theoretically by Heisenberg.[†] This spin difference is shown diagrammatically in Fig. 14, the extranuclear electrons being omitted. With hydrogen, isomers differing by virtue of parallel or antiparallel electronic, as distinct from nuclear, spin do not occur, since a parallel electronic spin would lead to an unstable molecule. This type of isomerization occurs, however, with certain other molecules (cf. ortho- and parahelium).

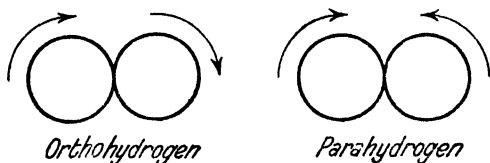


FIG. 14.

Ortho-para nuclear-spin modifications are possible in all diatomic molecules containing identical atoms with a nuclear spin. In general,[‡] molecules containing nuclei of odd atomic mass, such as hydrogen, follow the Fermi-Dirac statistics, the para, i.e. antiparallel, spin-form being restricted to even, and the ortho form to odd quantum states (zero is counted as an even number). On the other hand, molecules consisting of atoms of even mass numbers follow the Bose-Einstein statistics and occupy even rotational quantum levels in the ortho state and odd levels in the para state. Consequently, the stable form at low temperatures will be the para form for hydrogen and the ortho form for deuterium, since at low temperatures the molecules will be principally in the lowest (i.e. zero) quantum state.

Variation of the Ortho-Para Equilibrium with Temperature

In the case of hydrogen it appeared probable from the variation in the intensity of consecutive band-spectrum lines, due to even and to odd rotational levels, that, at room temperature, ortho molecules are approximately three times as abundant as para molecules. This has been verified by analysis. The corresponding figure for deuterium

[†] W. Heisenberg, *Z. Physik*, 1927, **41**, 239.

[‡] A. Farkas, L. Farkas, and P. Harteck, *Proc. Roy. Soc. 1934, A 144*, 481; see also A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, Cambridge, 1935, p. 159.

at ordinary temperatures involves a 2:1, in place of a 3:1, ortho-para ratio.

The equilibrium at various temperatures has been calculated by Giauque,[†] by Harkness and Deming,[‡] and by Farkas, Farkas, and Harteck[§] on the basis of the restriction of para and ortho molecules to even or odd levels in the way already discussed, i.e. parahydrogen or orthodeuterium to the levels 0, 2, 4,... and orthohydrogen or para-deuterium to the levels 1, 3, 5,...

The distribution of the molecules in the different rotational levels is governed by the Boltzmann law:

$$N_j = N_0 p_j e^{-E_j/kT}, \quad (i)$$

in which N_j is the number—out of the total number of molecules N_0 —in the rotational level j , E_j is the rotational energy of the molecule in this state in excess of the energy corresponding with the zero state, and p_j is the normal statistical weight $(2j+1)$ of the level multiplied by the appropriate spin factor. It can be shown that

$$E_j = \frac{j(j+1)h^2}{8\pi^2 J},$$

in which J is the moment of inertia. The spin factor for hydrogen, which follows the Fermi-Dirac statistics, will be $s(2s+1)$ for even (i.e. para) levels and $(s+1)(2s+1)$ for odd (i.e. ortho) levels, s being the nuclear spin of the atom. For deuterium (even nuclear mass, Bose-Einstein statistics), the values of these spin factors, like the levels occupied respectively by para and ortho molecules, will be reversed. For hydrogen, $s = \frac{1}{2}$, on a scale in which unity is $h/2\pi$, the spin of the deuterium atom being probably 1 on the same scale. The resulting values of p_j , which are required for insertion in equation (i), are consequently as follows:

TABLE 21

Molecule	Levels	s	Spin factor	Value of p_j
Parahydrogen . .	Even	$\frac{1}{2}$	$s(2s+1)$	$2j+1$
Orthohydrogen . .	Odd	$\frac{1}{2}$	$(s+1)(2s+1)$	$3(2j+1)$
Paradeuterium . .	Odd	1	$s(2s+1)$	$3(2j+1)$
Orthodeuterium . .	Even	1	$(s+1)(2s+1)$	$6(2j+1)$

[†] W. F. Giauque, *J. Amer. Chem. Soc.* 1930, **52**, 4808, 4816.

[‡] R. W. Harkness and W. E. Deming, *ibid.* 1932, **54**, 2850.

[§] Loc. cit. See also Weizel, 'Bandenspectren', *Wien-Harms Handbuch der experim. Physik*, 1933.

On the basis of the above the fraction of hydrogen molecules in the *para* state will be:

$$N_{\text{parahydrogen}} = \frac{\sum_{j=0,2,4,\dots} (2j+1)e^{-E_j/kT}}{\sum_{j=1,3,5,\dots} 3(2j+1)e^{-E_j/kT} + \sum_{j=0,2,4,\dots} (2j+1)e^{-E_j/kT}}$$

The corresponding fraction for orthodeuterium reduces to:

$$N_{\text{orthodeuterium}} = \frac{\sum_{j=0,2,4,\dots} 2(2j+1)e^{-E_j/kT}}{\sum_{j=1,3,5,\dots} (2j+1)e^{-E_j/kT} + \sum_{j=0,2,4,\dots} 2(2j+1)e^{-E_j/kT}}$$

The equilibrium percentages for parahydrogen† and orthodeuterium,‡ which are the stable modifications at low temperatures, are given for various temperatures in Table 22.

TABLE 22

<i>Temperature, ° Abs.</i>	<i>Percentage of parahydrogen at equilibrium</i>	<i>Percentage of orthodeuterium at equilibrium</i>
0	100	100
25	99.00	95.29
50	76.80	79.19
75	51.78	—
80	—	69.82
100	38.46	67.82
150	28.54	—
160	—	66.72
200	25.95	—
220	—	66.66
250	25.26	66.66
273	25.14	66.66
298	25.07	66.66

Under ordinary conditions interconversion of the two forms does not occur very readily in the gaseous state at low temperatures; and pure parahydrogen, corresponding with the equilibrium, is accordingly not easily produced by cooling alone. In the liquid or solid state, however, transformation does occur spontaneously with reasonable velocity,§ the reaction rate being somewhat greater in the solid than in the liquid phase and being practically independent of the temperature between 4° and 12° Abs. for the solid reaction and

† W. Giaque, loc. cit.

‡ H. L. Johnstone and E. A. Long, *J. Chem. Phys.* 1934, **2**, 389.

§ E. Cremer and M. Polanyi, *Z. physikal. Chem.* 1933, B **21**, 459.

between 14° and 20° for the liquid; but pure parahydrogen was not obtained even after storage for 145 hours at these temperatures, the best results observed corresponding with a gradual diminution of the orthohydrogen percentage from 75 to about 25 in the solid reaction and down to 33 in the liquid, in place of down to approximately zero concentration as required by the equilibrium.

This conversion in a condensed state suggests that the reaction might be expected to proceed in the presence of an adsorbent such as charcoal, which was the original method used by Bonhoeffer and Harteck† for the preparation of parahydrogen. Reaction in the presence of this adsorbent was found to occur rapidly at liquid hydrogen temperature; and the method forms the most effective way of obtaining pure parahydrogen or pure orthodeuterium.

Preparation of Parahydrogen

In Bonhoeffer and Harteck's experiments a silica adsorption vessel of about 50 c.c. capacity was filled with active charcoal and, after having been degassed at a red heat, the charcoal was cooled in contact with hydrogen, first to liquid air temperature and then to the temperature of liquid hydrogen. The above volume of charcoal adsorbed under these conditions some 8 litres of hydrogen in about a quarter of an hour; and the gas pumped off subsequently was substantially pure parahydrogen. The observed purity after various lengths of stay in the charcoal is given in Table 23.

TABLE 23

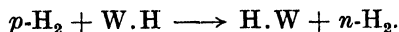
<i>Time, min.</i>	<i>Percentage of para- hydrogen in gas</i>
5	88
10	98.3
15	99.3
20	99.7
120	99.7

The activity of charcoal for the conversion first of all decreases with increasing temperature and subsequently increases, the temperature of minimum activity lying between 0° and 200° C. Metallic hydrogen-activating catalysts such as platinum or nickel are of less interest from the standpoint of the preparation of pure parahydrogen, since, although these readily catalyse the conversion at moderate temperatures, they are not very active at the low temperatures

† K. F. Bonhoeffer and P. Harteck, *Z. physikal. Chem.* 1929, B 4, 113.

required by the equilibrium conditions. The mechanism of the conversion in the presence of charcoal at low temperatures is obviously different from that on metallic catalysts at higher temperatures in which dissociation of the hydrogen molecule into atoms probably occurs on adsorption: indeed, Bonhoeffer, Farkas, and Rummel† considered this atomic adsorption to be the effective factor (see, however, next paragraph) in the high-temperature reaction on active metals.

Eley and Rideal‡ have examined the parahydrogen conversion on tungsten wires and films. Using the contact potential of the tungsten to measure the concentration of adsorbed oxygen, they showed that the catalytic effect was due to the oxygen-free tungsten surface. Roberts§ had shown that such a surface, on exposure to hydrogen, takes up a chemisorbed layer of hydrogen atoms, the layer being stable in that it does not evaporate below 800° Abs. It was accordingly argued that the parahydrogen conversion, which proceeds rapidly at 77° Abs., could not occur by means of a mechanism involving recombination and evaporation of chemisorbed hydrogen atoms. It was further found that the chemisorbed atomic hydrogen film would exchange with gaseous deuterium at low pressures at a rate similar to that observed for the conversion. It was therefore concluded that the parahydrogen conversion on tungsten takes place by an exchange of atoms between the stable chemisorbed atomic hydrogen film and parahydrogen molecules held in the van der Waals layer, namely, by the process



A similar mechanism seems operative for nickel, but results with palladium and platinum are less clear.||

In addition to this reaction on metallic catalysts, conversion may be induced by oxide catalysts on which the activated adsorption of hydrogen takes place.¶ Conversion also occurs spontaneously at high temperatures, for instance at 600° or above, the mechanism probably involving interaction with hydrogen atoms produced by thermal dissociation.

† K. F. Bonhoeffer, A. Farkas, and K. W. Rummel, *ibid.* 1933, B 21, 225.

‡ D. D. Eley and E. K. Rideal, *Proc. Roy. Soc.* 1941, A 178, 429; D. D. Eley, *ibid.*, p. 452.

§ J. K. Roberts, *Trans. Faraday Soc.* 1939, 35, 941.

|| A. and L. Farkas, *J. Amer. Chem. Soc.* 1942, 64, 1594.

¶ H. S. Taylor and A. Sherman, *Trans. Faraday Soc.* 1932, 28, 247.

Pure orthodeuterium may be prepared by a similar method to that described above for parahydrogen, namely, by low-temperature desorption of deuterium from charcoal.†

Magnetic Properties and Conversion by Paramagnetic Substances

The para and ortho forms of the hydrogen molecule differ in magnetic properties, since the portion of the magnetic moment due to nuclear spin is zero in para molecules with equal opposed or cancelling spins, whereas in ortho molecules, with similar-sense nuclear spins, this moment should be twice that due to the individual nuclear spin.

It is found, moreover, that extraneous paramagnetic substances in general possess the power of normalizing mixtures of the hydrogen isomers. Thus, conversion takes place readily in the presence of paramagnetic molecules such as oxygen, nitric oxide, or nitrogen peroxide, while diamagnetic substances such as nitrous oxide, ammonia, or sulphur dioxide have been shown experimentally to be inactive. It is probable that the transition is caused by the perturbation which the hydrogen molecule experiences during collision in the inhomogeneous magnetic field of the collision partner, this perturbation partly freeing the normally forbidden $p \rightleftharpoons o$ transition, so that, in a certain fraction of the collisions, a transition from the para to the ortho state, or vice versa, becomes possible.‡ In this connexion it may be noted that the slow spontaneous conversion observed in ortho-para mixtures may itself be caused by the magnetic moment of the ortho molecules, this moment, however, being very small in comparison with that of, for instance, oxygen, and accordingly leading to a very small reaction rate.

TABLE 24

Ion	Relative velocity of para-ortho conversion	Magnetic moment of ion	
		van Vleck§	Bose
Zn ²⁺	0	0	0
Cu ²⁺	18.7	3.53	1.73
Ni ²⁺	25.2	5.56	2.83
Co ²⁺	57.5	6.56	3.87
Fe ²⁺	63.2	6.54	4.90
Mn ²⁺	100.0	5.92	5.92

† L. Farkas and L. Sandler, *J. Amer. Chem. Soc.* 1940, **62**, 2877.

‡ L. Farkas and H. Sachsse, *Z. physikal. Chem.* 1933, B **23**, 19; E. Wigner, *ibid.*, p. 28.

§ *Electric and Magnetic Susceptibilities*, Oxford, 1932.

|| *Loc. cit.*, p. 285.

The relative effect of paramagnetic substances of various magnetic moments is exemplified by Table 24, which summarizes results obtained by Farkas and Sachsse with solutions containing paramagnetic ions, principally of the iron group.

General Properties of the Isomers

It should be emphasized that, while pure parahydrogen is readily obtainable, orthohydrogen has not yet been prepared in a pure state owing to the equilibrium limit of 75 per cent. of the ortho form; consequently the exact properties of pure orthohydrogen, other than those which can be deduced from those of mixtures of the isomers, are unknown.

Parahydrogen has a slightly lower melting- and boiling-point than normal hydrogen and consequently than orthohydrogen. It melts at 13.82° Abs. and boils at 20.26° , the corresponding figures for normal hydrogen being 13.92° and 20.38° : accordingly parahydrogen has a higher vapour pressure at a given temperature than normal hydrogen. Values† for the vapour pressure at various temperatures are given in Table 25.

TABLE 25

Temperature ° C.	Vapour pressures, in mm. Hg	
	Parahydrogen	Normal hydrogen
—253	732.9	708.2
—254	534.5	515.5
—255	381.7	365.0
—256	261.7	250.5
—257	174.0	166.7
—258	108.7	103.5

These differences would, of course, be accentuated if the comparison could be made with pure orthohydrogen in place of the normal mixture. The ortho and para forms of hydrogen also differ in specific heat (and consequently in internal energy at a given temperature) and in conductivity. A discussion of these points is omitted for reasons of space; for further details reference may be made to Farkas's monograph.

† K. F. Bonhoeffer and P. Harteck, loc. cit.; W. H. Keesom, A. Bijl, and H. van der Horst, *Proc. K. Acad. Wet. Amsterdam*, 1931, **34**, 1223. See also A. Farkas, *Parahydrogen, Orthohydrogen and Heavy Hydrogen*, Cambridge, 1935.

Analysis of Ortho-Para Hydrogen Mixtures

The method most frequently used is due to Bonhoeffer and Har-teck† and depends on the above-mentioned difference in conductivity. The ortho-para mixture to be analysed is admitted at a known pressure to a vessel containing a metallic filament heated by a constant current, when the temperature of the filament (which is measured by its resistance) will, in consequence of the lower conductivity of orthohydrogen, vary with the concentration of this species in the mixture, i.e. the filament temperature for a given current will be the higher the higher the concentration of orthohydrogen. The apparatus has, of course, to be calibrated empirically with known mixtures. The usual temperature is about 170° Abs., which corresponds with the greatest difference in the conductivity of ortho- and parahydrogen. Similarly, the pressure employed is usually in the range 20–40 mm., in which region the variation of the emission of heat with the pressure is relatively low. The method has been modified by A. Farkas,‡ for use at very low pressures, by adjusting the pressure during the measurement so as to give constant wire temperatures; and it can, in this form, be used for the analysis of a gas volume as low as several cubic millimetres, the pressure employed being of the order of 0.05 mm. Hg. Another micropirani gauge, working at 50 mm. pressure, has been developed by Bolland and Melville.§ On account of the relatively high pressure used this latter gauge is comparatively free from troubles due to variations in the accommodation coefficient.

DEUTERIUM (²H OR D)

Indications of the existence of this isotope were obtained in 1931 by Urey, Brickwedde, and Murphy|| who, in the course of an examination of the optical spectrum of residues from liquid hydrogen, detected shifts in the Balmer lines, corresponding with displacements which could be predicted theoretically if a heavier hydrogen isotope of mass 2 were present. The intensity of these secondary lines was, moreover, increased by further fractionating the hydrogen and testing the heavier fraction. It should be noted that the isotopic shift in question—which is capable of exact calculation in the special case of

† *Sitzungsber. preuss. Akad. Wiss., Phys.-Math. Kl.* 1929, 103.

‡ *Z. physikal. Chem.* 1933, B 22, 344.

§ J. L. Bolland and H. W. Melville, *Trans. Faraday Soc.* 1937, 33, 1316.

|| H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Phys. Rev.* 1932, 39, 164, 864.

hydrogen—is an electronic effect influencing the atomic spectrum and is distinct from the general effect of a change of nuclear mass on the moment of inertia of the molecule and consequently on the frequency of the fine-structure lines in the molecular band spectrum. The existence of a heavier hydrogen isotope was also predicted by Birge and Menzel† on the basis of discrepancies in the atomic weight of natural hydrogen.

The preparation of the pure isotope does not proceed readily by the fractional distillation either of hydrogen itself or of water. Separation of deuterium from hydrogen has, however, been carried out by multi-stage diffusion,‡ also by thermal diffusion in a Clusius tube (see p. 37). The practical preparation of pure deuterium was greatly facilitated by the observation of Washburn and Urey§ that water in an electrolytic cell, which had been operated for a considerable time, contained an appreciably larger concentration of deuterium than ordinary water and that, in general, if ordinary water is electrolysed the light water is preferentially decomposed and the deuterium (as heavy water) is progressively concentrated in the residue.

Early work confirming and extending the results of this electrolytic method was carried out by G. N. Lewis and R. T. Macdonald,|| who concentrated electrolytically 20 litres of water derived from an electrolytic cell down to 0.5 c.c., with suitable additions of alkali and redistillation at various stages of the electrolysis. The density of the final water rose to 1.073 times that of ordinary water under similar conditions, corresponding with a final deuterium content of about 66 per cent.; and it was estimated that a further reduction of the final volume to one-quarter should give a 99 per cent. deuterium oxide concentration. No accumulation of the heavier oxygen isotope was observed.

A detailed description of experimental technique has been given by Taylor, Eyring, and Frost.¶ The starting material consisted of old electrolyte from commercial electrolytic cells, which was first distilled to remove the original alkali. Sodium hydroxide was then added to make a 0.5 molar solution; and this was further electrolysed

† R. T. Birge and D. H. Menzel, *ibid.* 1931, **37**, 1669.

‡ H. Harmsen, G. Hertz, and W. Schütze, *Z. Phys.* 1934, **90**, 703.

§ E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.* 1932, **18**, 496.

|| *J. Chem. Phys.* 1933, **1**, 341.

¶ H. S. Taylor, H. Eyring, and A. A. Frost, *ibid.*, p. 823.

in a battery of 210 small glass cells (hydrometer jars), each 4 cm. in diameter and 25 cm. high, provided with strip nickel electrodes and immersed in a cooling-tank containing water. The battery was, for convenience of current supply, subdivided into units of 30 cells each. The electrolyte was reduced to about one-sixth of its original volume, the process usually taking about three days, after which it was removed and replaced by a fresh charge. The concentrated electrolyte from this first electrolysis was partly neutralized to the carbonate by bubbling carbon dioxide through it, using fuchsin as an indicator. It was then distilled and the distillate added to a further group of cells containing water of the same grade and still containing all the sodium hydroxide originally added. In the course of three successive electrolyses water of $D_4^{20} = 1.001$ was obtained, corresponding with an approximately 2.5 per cent. concentration of D_2O .

From this stage onwards the hydrogen evolved contains an appreciable concentration of deuterium. It was therefore burnt at a jet, the water produced being added to appropriate cells. The progressive concentration of D_2O is summarized in Table 26.

TABLE 26

<i>Water from</i>	<i>Volume electrolysed (at start)</i>	D_4^{20}	<i>Percentage of D_2O</i>
1st electrolysis	610 gallons	0.998	—
2nd ,,	90 gallons	0.999	0.5
3rd ,,	52 litres	1.001	2.5
4th ,,	10.15 litres	1.007	8
5th ,,	2.00 litres	1.031	30
6th ,,	420 c.c.	1.098	93
7th ,,	82 c.c.	1.104	99

The course of the enrichment† can be expressed mathematically as follows. If x_1 and x_2 are the total amounts of hydrogen and deuterium present in the electrolyte at any stage, then the relative rate of change in x_1 and x_2 is given by

$$d \log_e x_1 = \alpha . d \log_e x_2, \quad (i)$$

in which α is the so-called separation factor representing the relative ease of electrolytic liberation of hydrogen and deuterium under equivalent conditions, i.e. the ratio between the rates of production of hydrogen and of deuterium which would exist if the amounts of each isotope in an electrolyte were the same.

† See A. Farkas, *Light and Heavy Hydrogen*, Cambridge, 1935, p. 125.

If V is the volume of the electrolyte, the concentrations of hydrogen and of deuterium are

$$(H) = \frac{x_1}{V} \quad \text{and} \quad (D) = \frac{x_2}{V}.$$

Further, if V_0 , $(H)_0$, and $(D)_0$ represent respectively the volume at the start of the electrolysis and the original concentrations of hydrogen and of deuterium, equation (i) may be expressed in the form:

$$\frac{(H)_0}{(H)} \left[\frac{(D)}{(D)_0} \right]^\alpha = \left(\frac{V_0}{V} \right)^{\alpha-1}. \quad (ii)$$

Equation (ii) allows the calculation of the reduction in the volume of the electrolyte which is necessary in order to produce, from ordinary water, heavy water of a given deuterium content. Some figures for this, calculated on the basis of a value of 5 for the separation factor, are given in Table 27. The original deuterium content is assumed to have its normal value, i.e. 0.02 per cent. of the total hydrogen in the original water.

TABLE 27

<i>D₂O concentration. Per cent.</i>	<i>Ratio of original volume to final volume</i>
10	2,400
50	21,000
75	41,000
90	66,000
99	130,000

The value of the separation factor varies somewhat with the nature, and even with the state, of the electrodes. It is also affected by whether an alkaline or an acid electrolyte is used; but it does not change greatly with the concentration of the deuterium. Topley and Eyring† give the following values of α for various cathodes.

TABLE 28

<i>Cathode</i>	<i>Values of α</i>	
	<i>Alkaline electrolyte</i>	<i>Acid electrolyte</i>
Pb	7.2-7.4	6.2-6.5
Pt	6.5-7.6	3.4-6.4
Fe	6.9-7.6	—
Ni	5.5	—
Cu	6.8	5.5-5.8
Ag	5.3-5.8	5.6-6.0
Hg	—	c. 2.8

† B. Topley and H. Eyring, *J. Chem. Phys.* 1934, 2, 217.

Preparation of Deuterium from Heavy Water

If, as is usually the case, only small quantities of deuterium are required, the most convenient method is that due to A. and L. Farkas,[†] in which a tungsten filament, heated electrically to about $1,000^{\circ}$, is used to decompose the water. The tungsten oxide formed is volatile at the working temperature and distils from the filament, exposing a fresh surface. It is stated that a wire 0.2 mm. in thickness

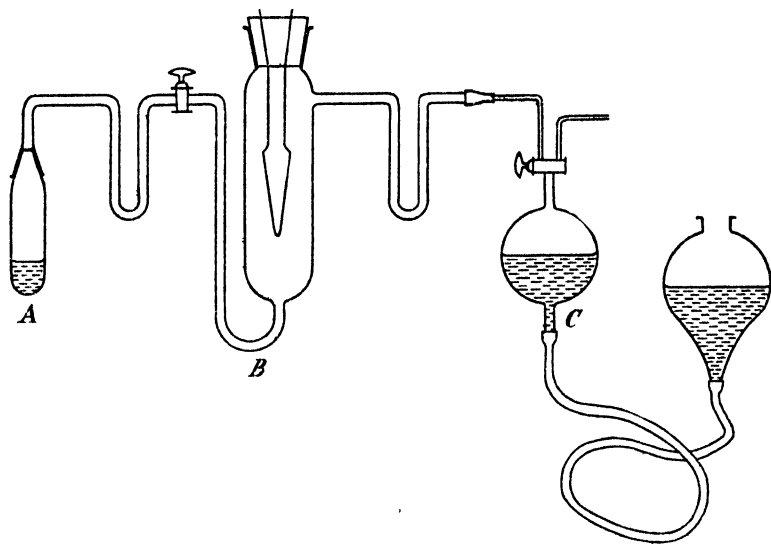


FIG. 15.

and 20 cm. long ordinarily gives about 30 c.c. of gas (at N.T.P.) before burning through. The apparatus is shown in Fig. 15, in which *A* is a small reservoir containing the heavy water, *B* is the decomposition chamber containing the tungsten filament, and *C* is a Töpler pump or its equivalent. Before beginning the preparation it is necessary to remove traces of adsorbed water, as far as possible, by heating the apparatus and by degassing the filament at about $2,000^{\circ}$, the whole apparatus being connected to a high-vacuum system during this preliminary treatment.

For somewhat larger quantities of deuterium, zinc forms a convenient decomposing agent; but other metals, e.g. sodium, may also be used. An apparatus suitable for use with zinc is illustrated in Fig. 16. This is conveniently made of pyrex glass, with the exception

[†] *Proc. Roy. Soc.* 1934, A 144, 467.

of the decomposition tube, *A*, which is of silica and is attached to the pyrex parts by ground joints. Before starting the preparation, the apparatus is connected to a high-vacuum pump and degassed, as before, by passing a flame over its surface. It will be seen that the heavy water, which is initially introduced into *C*, can (after being frozen in liquid air during the initial evacuation) be distilled over the heated zinc either in the direction *C* to *B* or *B* to *C*, without loss

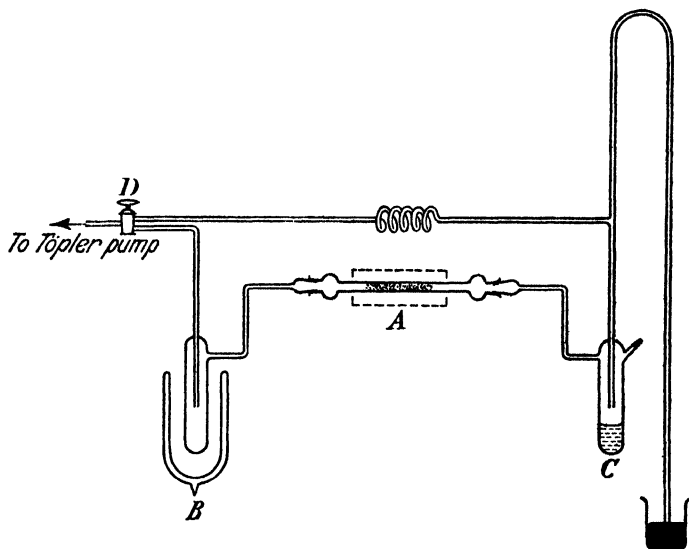


FIG. 16.

of heavy water by passage to the pump, by placing the Dewar flask containing liquid air either around the trap *B* or the trap *C* and by suitably turning the three-way tap, *D*, the uncooled trap being immersed in a beaker of water kept at a temperature sufficient to give a convenient rate of distillation. The zinc is heated by means of a flame. The rate of decomposition can be followed by the fall of the mercury in the Töpler pump.

The HD Molecule

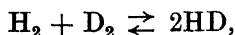
It should be noted that, in addition to hydrogen and deuterium, the intermediate molecule, HD, also exists. This has no ortho-para varieties.

The equilibrium

$$K = \frac{[\text{HD}]^2}{[\text{H}_2] \times [\text{D}_2]},$$

H

corresponding with the equation



has been calculated from first principles by Urey and Rittenberg,† who derive the approximate relationship

$$\log K = -\frac{34}{T} + 0.6276$$

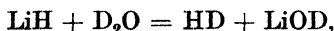
for the variation of the equilibrium constant with temperature.

In a later paper‡ the equilibrium was examined experimentally and figures for the relative abundance of the three forms were obtained which on the whole agree with the above equation. It will be seen from the typical results collected in Table 29 that, although the value of the constant itself does not vary greatly with the temperature, the relative abundances change a good deal as the temperature is raised from 25° to about 470°. The abundances at 397° are mean values.

TABLE 29

Temp. °C.	Relative abundances			K (obs.)	K (calc.)
	D ₂	HD	H ₂		
25	1	20.8	132	3.3	3.2
397	1	13.2	46.7	3.0	3.8
468	1	2.7	1.9	3.8	3.9

A chemical method for the direct preparation of HD, involving the reaction



has also been described.§ The gas evolved showed strong absorption bands, due to HD, in the ultra-violet absorption spectrum.

The existence of this intermediate molecule necessarily influences the simplicity of the variation of the physical properties of deuterium-hydrogen mixtures with their deuterium or hydrogen content: further, since equilibrium is established quickly only at high temperatures or in contact with a catalyst, some ambiguity also exists as to whether a given mixture has attained equilibrium. These factors have, however, only a slight weight in practice, since the properties of HD are roughly intermediate between those of H₂ and D₂. This can be shown,

† H. C. Urey and D. Rittenberg, *J. Chem. Phys.* 1933, **1**, 137.

‡ D. Rittenberg, W. Bleakney, and H. C. Urey, *ibid.* 1934, **2**, 48.

§ H. Beutler, G. Brauer, and H. O. Jünger, *Naturwiss.* 1936, **24**, 347.

for instance, by the substantial identity of almost any physical property of such a mixture before and after the establishment of equilibrium by contact with a platinum catalyst. The determination of the properties of pure deuterium or pure hydrogen is, of course, unaffected.

PHYSICAL PROPERTIES OF DEUTERIUM

Some of the physical constants of deuterium are collected in Table 30, in which, for comparison, the corresponding figures for hydrogen have also been inserted. These relate, as far as the molecular properties are concerned, to *n*-deuterium and *n*-hydrogen and not to separate isomers.

TABLE 30

	<i>Deuterium</i>	<i>Hydrogen</i>
Triple point, † ° K.	18.71	13.92
Boiling-point, ° K.	23.59	20.38
Latent heat of fusion, ‡ cal./mole	52.3	28.0
Nuclear spin, in units of $h/2\pi$	1	$\frac{1}{2}$

The variation of the latent heat of vaporization (or the latent heat of sublimation in the case of the solid phase) with the temperature, as calculated by Scott, Brickwedde, Urey, and Wahl from their vapour-pressure curves, is as follows:

TABLE 31

<i>Temperature, ° K.</i>	<i>Latent heats of vaporization, in cal. per mole</i>	
	<i>Hydrogen</i>	<i>Deuterium</i>
13.92	245.7 (solid)	—
	217.7 (liquid)	340.8 (solid)
16.43	—	349.6 "
18.182	—	354.5 "
18.58	218.7 (liquid)	355.4 "
		303.1 (liquid)
18.953	—	304.0 "
19.330	—	304.8 "
20.334	—	306.8 "
20.38	215.9 (liquid)	—

It will be noted that the temperature (18.58° K.) taken in the table as the triple point of deuterium differs slightly from that given above.

† F. G. Brickwedde, R. B. Scott, and H. S. Taylor, *J. Chem. Phys.* 1935, **3**, 653.

‡ R. B. Scott, F. G. Brickwedde, H. C. Urey, and M. H. Wahl, *ibid.* 1934, **2**, 454.

Vapour Pressure

The vapour pressure of solid and of liquid deuterium has been measured by Lewis and Hanson† and by Scott, Brickwedde, Urey, and Wahl.‡ Owing probably to drifts due to ortho-para conversion at the low temperatures, the figures given by these two groups of workers differ slightly. Some representative values, due to the latter group, are as follows:

TABLE 32

<i>Temperature</i>	<i>Vapour pressure, in mm. Hg</i>	
	<i>Hydrogen</i>	<i>Deuterium</i>
Triple point of H ₂ . .	54	5.8
Triple point of D ₂ . .	458	130
Boiling-point of H ₂ . .	760	250

Pressures at some accurately determined intermediate temperatures are given in Table 33.

TABLE 33

<i>Temperature, ° K.</i>	<i>Vapour pressure, in mm. Hg</i>	
	<i>n-H₂</i>	<i>n-D₂</i>
15.188	106.1 (liquid)	14.2 (solid)
16.463	190.3 "	35.0 "
17.479	287.0 "	65.5 "
18.182	372.4 "	97.7 "
18.945	484.9 "	142.4 (liquid)
18.953	486.0 "	143.2 "
19.167	521.7 "	157.1 "
19.330	550.0 "	168.5 "
19.969	672.0 "	218.5 "
20.334	749.8 "	252.0 "

Brickwedde, Scott, and Taylor§ have calculated the differences in vapour pressure between the ortho-para spin isomers. These are given in Table 34, in which *n*-D₂ represents the room-temperature equilibrium mixture (66.7 per cent. orthodeuterium) and *e*-D₂ is the equilibrium mixture at 20° K. All vapour pressures, or differences in these, are in mm. Hg.

† G. N. Lewis and W. T. Hanson, *J. Amer. Chem. Soc.* 1934, **56**, 406.

‡ *Phys. Rev.* 1934, **45**, 565 and loc. cit.

§ Loc. cit.

TABLE 34

Temperature, ° K.	P ($n\text{-D}_2$)	ΔP ($e\text{-D}_2 - n\text{-D}_2$)	ΔP ($o\text{-D}_2 - p\text{-D}_2$)
15	12.6	0.3	0.8
18	88.2	1.6	4.9
20	221.0	3.3	10.4

The third and fourth columns give, respectively, the vapour-pressure differences between $e\text{-D}_2$ and $n\text{-D}_2$ and between $o\text{-D}_2$ and $p\text{-D}_2$, the pressure of the ortho form being greater than that of the para isomer. It will be seen from the corresponding figures for light hydrogen (p. 91) that, with this, the para form has the higher vapour pressure.

Ortho- and paradeuterium, like ortho- and parahydrogen, also differ slightly in triple point and boiling-point: thus, while pure paradeuterium cannot be prepared for direct comparison, the triple point of $e\text{-D}_2$ is 18.67° K. and that of $n\text{-D}_2$ is 18.71° .

Specific Heat and Conductivity

These properties are of considerable practical as well as theoretical interest, since a widely used method of analysis of hydrogen-deuterium mixtures consists in measurements of conductivity based on the loss of heat by a heated filament suspended (as in the analysis of ortho- and parahydrogen mixtures) in the mixture of deuterium and hydrogen. The specific heats are complicated by the existence of many different hydrogen molecules ($o\text{-D}_2$, $p\text{-D}_2$, HD, $o\text{-H}_2$, $p\text{-H}_2$); and, for a detailed discussion, reference may be made to Farkas's monograph† and to the experimental measurements, for instance, of Clusius and Bartholomé.‡

In connexion with the technique used for the analysis by measuring the loss of heat from a filament, it may be noted that A. and L. Farkas's micro-method,§ already referred to under parahydrogen, only requires samples of 0.002 c.c. of gas. Practical details for the construction of apparatus have also been given by Melville, Bolland, and Roxburgh.||

† *Light and Heavy Hydrogen*, pp. 161-5.

‡ K. Clusius and E. Bartholomé, *Naturwiss.* 1934, **22**, 297; *Z. Elektrochem.* 1934, **40**, 524.

§ *Proc. Roy. Soc.* 1934, A **144**, 467.

|| H. W. Melville, J. L. Bolland, and H. L. Roxburgh, *ibid.* 1937, A **160**, 384.

Zero-point Energies

The relative values of these constants for the two hydrogen isotopes and for the intermediate molecule, HD, are of interest in connexion with the usually lower reaction rate of molecular deuterium compared with that of hydrogen. The following values, in calories per mole, have been calculated by Urey and Rittenberg† and by Birge, Hyman, and Jeppesen.‡

TABLE 35

<i>Molecule</i>	<i>Zero-point energies</i>			
H ₂	6,176 (Urey and Rittenberg)	6,134 (Birge and co-workers)		
HD	5,359 " "	5,323 " "		
D ₂	4,387 " "	4,357 " "		

This difference in zero-point energies extends also to deuterium and hydrogen compounds generally. For instance, the zero-point energies of H³⁵Cl and of D³⁵Cl have been calculated to be 4,214 and 3,030 cal. per mole respectively.

CHEMICAL PROPERTIES OF DEUTERIUM

As is the case for all isotopes of the same element, the chemical properties of deuterium will, in general, be the same as those of hydrogen: accordingly, deuterium can function in every way as hydrogen, taking the place of hydrogen in molecules of all types and forming completely equivalent compounds.

The intensity of these chemical properties, including what is generally known as the affinity—which is reflected, for instance, in the reaction speed and in the position of equilibria—will, however, be influenced, far more than for any other pair of isotopes, by factors such as the large difference in the zero-point energies and by the abnormally large mass ratio (2 to 1) of the two isotopes.

A simple example of a difference in reaction rates is to be found in the relative velocities of chemisorption of deuterium and hydrogen on metallic and other surfaces, including diffusion through metals. Thus, A. and L. Farkas§ found that the rate of diffusion of deuterium through palladium foil (in which the controlling factor, in the steady state, is the rate of adsorption of gas at the metal surface) takes

† H. C. Urey and D. Rittenberg, *J. Chem. Phys.* 1933, **1**, 139.

‡ R. T. Birge, H. H. Hyman, and C. R. Jeppesen, *Nature*, 1930, **123**, 277, 462; Hyman, *Phys. Rev.* 1930, **36**, 187.

§ *Proc. Roy. Soc.* 1934, A **144**, 467.

place more slowly at low or moderate temperatures than the corresponding diffusion of hydrogen, probably principally as a result of zero-point energy differences rather than of factors inherent in the difference of mass. Similar differences in the relative rates of adsorption of deuterium and hydrogen on finely divided platinum have also been observed† in the temperature range -80° to $+50^{\circ}$. At higher temperatures, for instance, above 300° in the case of palladium, this difference in the adsorption rate tends to vanish. Pace and Taylor‡ also report an approximately equal adsorption rate for deuterium and hydrogen on chemisorptive oxide catalysts such as Cr_2O_3 or zinc chromite. For the probable nature of the change in the rate-controlling factor at high temperatures, reference should be made to Farkas's paper.

Differences in reaction rates also occur in catalytic hydrogenation with deuterium or with hydrogen. Where the reaction is of such a type that the complication of deuterium-hydrogen exchange with hydrogen in the substance hydrogenated does not exist, such as in the deuteration or hydrogenation of nitrous oxide on a nickel filament§ or in the catalytic combination of hydrogen or deuterium and oxygen, a ratio in the respective reaction rates of hydrogen and of deuterium was observed which was considerably higher than could be accounted for by a collision factor involving the mass of the atoms ($\sqrt{2}$), pointing to differences in reaction rates again due probably to differences in zero-point energies. Some typical velocity ratios, calculated by Melville for pure hydrogen and pure deuterium, are given in Table 36.

TABLE 36

Reaction	Temperature, $^{\circ}\text{C}$.	Ratio of rate of reaction of hydrogen to rate of reaction of deuterium
$\text{H}_2 + \text{N}_2\text{O}$	159	2.44
	192	2.10
$\text{H}_2 + \text{O}_2$	177	2.42
	226	2.09
	255	2.31

It may be noted that the calculated difference in the apparent activation energies for the hydrogen and the deuterium reaction has,

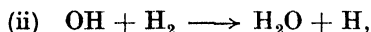
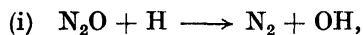
† E. B. Maxted and C. H. Moon, *J. Chem. Soc.* 1936, 1542.

‡ J. Pace and H. S. Taylor, *J. Chem. Phys.* 1934, 2, 570.

§ H. W. Melville, *J. Chem. Soc.* 1934, 797, 1243.

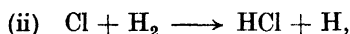
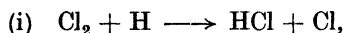
both for the reduction of nitrous oxide and for the interaction with oxygen, approximately the same value (0.7 kg.-cals.) as the zero-point energy difference of the adsorption complexes Ni—H and Ni—D, calculated from spectroscopic data; and the increased rate of reaction of the Ni—H complex may thus be largely due to its higher zero-point energy.

The importance of zero-point energy factors appears to be confirmed by further experiments of Melville, in which the interaction of nitrous oxide and hydrogen (or deuterium) was caused to take place by employing atomic hydrogen or deuterium produced photochemically by the mercury vapour resonance method (see p. 82). It is known† that this reaction consists of the two steps:



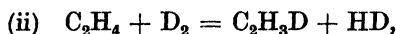
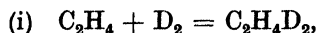
of which the first is the slower or rate-controlling process. With the deuterium or hydrogen in the atomic state, in which the zero-point energy does not contribute to the energy of activation, the rate of reaction with deuterium was equal to that with hydrogen.

This reaction may be contrasted with the somewhat similar two-stage reaction of atomic hydrogen or deuterium with chlorine:



in which the second, not the first, stage is the slow reaction and for which Farkas‡ has shown that the process becomes considerably slower if deuterium is substituted for hydrogen.

As would be expected from the operation of exchange effects the catalytic deuteration of compounds containing hydrogen is complicated by substitution. Thus, A. and L. Farkas,§ who studied the mechanism of the hydrogenation (with deuterium and with hydrogen) of ethylene in the presence of platinum at temperatures from 0° to 236°, observed the reactions:



and probably also further exchange. The ratio of exchange to

† H. W. Melville, *Proc. Roy. Soc.* 1933, A 142, 524; *Trans. Faraday Soc.* 1933, 29, 1255.

‡ A. and L. Farkas, *Naturwiss.* 1934, 22, 218.

§ A. and L. Farkas, *J. Amer. Chem. Soc.* 1938, 60, 22; see also A. Farkas, L. Farkas, and E. K. Rideal, *Proc. Roy. Soc.* 1934, A 146, 630.

hydrogenation increased with the temperature, as is shown in Table 37; but no exchange between deuterium and ethane was obtained up to 300°.

TABLE 37

<i>Temperature, ° C.</i>	<i>Ratio of exchange to hydrogenation</i>
25	0.02
54	0.08
79	0.5
100	0.7
120	1.7
146	2.3
187	6.1
235	13.1

As in the catalytic N_2O -hydrogen reaction discussed above, the addition reaction takes place, at low temperatures, more rapidly with ordinary hydrogen than with deuterium; but this hydrogen-deuterium rate ratio decreases as the temperature is raised and, at high temperatures, the catalytic addition of deuterium may take place as fast as, or even faster than, the addition of hydrogen. This change in the relative reaction velocities with hydrogen and deuterium as the temperature is increased becomes even more pronounced if the exchange and addition velocities are not separated, probably by reason of the greater temperature coefficient of the deuterium exchange reaction. Thus, Pease and Wheeler,[†] who merely compared the gross absorption of deuterium and of hydrogen by ethylene, found that, in the presence of a copper catalyst, the ratio of the hydrogen-deuterium rates was 1.59 at 0°, 1.34 at 184°, and 1.04 at 306°; and Klar,[‡] using an iron catalyst, observed at a reaction temperature of 100° a reversal from the usually slower rate with deuterium to a rate faster than that with hydrogen. For the somewhat similar hydrogenation of benzene, reference may be made to the work of A. and L. Farkas[§] and of Horiuti, Ogden, and Polanyi.||

Hydrogenation with deuterium, apart from its relative velocity compared with hydrogen, resembles hydrogenation with ordinary hydrogen in possessing a positive temperature coefficient for the

[†] R. N. Pease and A. Wheeler, *J. Amer. Chem. Soc.* 1935, **57**, 1145.

[‡] R. Klar, *Z. physikal. Chem.* 1934, **A 27**, 319.

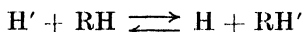
[§] *Trans. Faraday Soc.* 1937, **33**, 827.

|| J. Horiuti, G. Ogden, and M. Polanyi, *Trans. Faraday Soc.* 1934, **30**, 663.

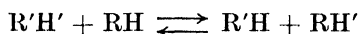
reaction rate at low temperatures and a negative coefficient at higher temperatures.

EXCHANGE REACTIONS

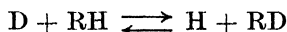
Since deuterium can be regarded chemically as ordinary hydrogen labelled by reason of its mass, deuterium-hydrogen exchange reactions provide valuable evidence for cases in which a change in the individuality of the ordinary hydrogen atoms in a molecule occurs normally. Thus, if H and H' represent distinct individual hydrogen atoms, the occurrence of an exchange of either of the types



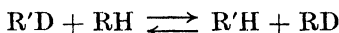
or



would not be detectable in the absence of such a label either for H' or H; but, if deuterium is used for H', the reaction becomes



or



and the exchange can easily be followed. An alternative method of labelling the one or the other hydrogen atom would be to use radioactive hydrogen: further, it is probable that exchange processes which can be shown to occur by using deuterium or an alternative form of labelled hydrogen also take place in ordinary systems in which the hydrogen present is substantially all of the same type, although in such cases the process cannot be detected.

CONDITIONS GOVERNING EXCHANGE

In general, molecular deuterium (or molecular hydrogen) does not readily enter into exchange reactions. For instance, gaseous deuterium may, at low or moderate temperatures, be left for long periods in contact with ordinary liquid or gaseous water without exchange, the same being true for molecular hydrogen in contact with heavy water or with HDO.

If, however, the temperature is raised so that an appreciable concentration of free deuterium or hydrogen atoms results, exchange will usually occur. The same effect can often be obtained by introducing a suitable hydrogenation catalyst, which may probably be regarded as a source of dissociated hydrogen or deuterium. Exchange also takes place in many cases in liquid systems containing deuterium or hydrogen ions, which may be present in the hydrated form (D_3O^+ or H_3O^+).

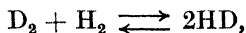
The above three conditions which are conducive to exchange can thus be classified as applying to:

- (i) Systems containing free hydrogen or deuterium atoms.
- (ii) Systems containing hydrogenation catalysts.
- (iii) Systems containing hydrogen or deuterium ions.

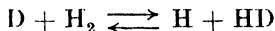
(i) *Exchange with Deuterium or Hydrogen Atoms*

In addition to the thermal production of deuterium or hydrogen atoms at high temperatures (effectively above 600°), atomic deuterium or hydrogen may be produced in a discharge tube or photochemically by the mercury-sensitized radiation resonance method already described. In all these cases, as well as in the catalysed exchange dealt with in the next section, exchange can be effected even in cases (e.g. methane or the methyl group) for which ionic exchange in solution fails.

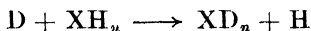
The equilibrium in the simplest exchange reaction



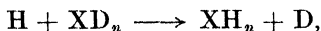
in which the reaction course may, save for direct atomic combination, be regarded as



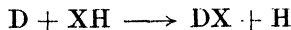
has already been discussed. Similar exchanges of the type



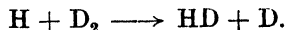
in which XH_n may, for instance, be H_2O , NH_3 , or CH_4 , or the reversed exchange



have also been extensively investigated both at high temperatures and with atomic deuterium produced in other ways. Thus, the mercury photo-sensitized exchange reactions of deuterium with water, ammonia, and methane have been studied by A. Farkas and H. W. Melville.† With ammonia and methane, it was possible to show from the kinetics that, above 300°, the reaction proceeded by the chain mechanism



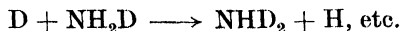
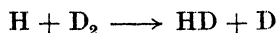
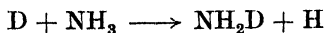
followed by



In the case of a molecule containing more than one hydrogen atom,

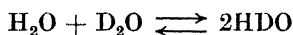
† *Proc. Roy. Soc.* 1936, A 157, 625; see also H. S. Taylor, K. Morikawa, and W. S. Benedict, *J. Amer. Chem. Soc.* 1935, 57, 383.

progressive deuteration, until all the hydrogen atoms have been replaced by deuterium, proceeds by a similar chain,† e.g.



A similar deuteration of phosphine also occurs.‡ For the exchange of deuterium atoms, from a Wood's discharge tube, with water, ammonia, and acetylene, reference may be made to the work of Geib and Steacie.§

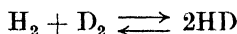
Exchange reactions such as



have been shown to take place similarly both at high temperatures and in a discharge tube, also by photochemical activation.||

(ii) Catalytic Exchange

As has already been mentioned, mixtures of molecular hydrogen and molecular deuterium are stable at low temperatures save in the presence of a catalyst (Ni, Pt, etc.). Their interaction in the presence of nickel has been studied by A. and L. Farkas¶ and by Fajans.†† By comparing the reaction



on metallic catalysts with the ortho-para hydrogen conversion, it appears probable that both reactions take place by the same mechanism, the rate-determining step being the supply of deuterium or hydrogen atoms. The reaction also takes place on hydrogenating catalysts of oxide type (Cr_2O_3 , etc.) and even on active carbon,‡‡ provided that this has been previously well degassed, e.g. for several weeks at 900–950°.

Horiuti and Polanyi,§§ also Gould and Bleakney,|||| have shown that deuterium does not exchange with water at room or moderate temperatures except in the presence of a catalyst such as platinum black.

† *J. Chem. Soc.* 1936, 26.

‡ H. W. Melville, J. L. Bolland, and H. L. Roxburgh, *Proc. Roy. Soc.* 1937, A **160**, 834.

§ K. H. Geib and E. W. R. Steacie, *Z. physikal. Chem.* 1935, B **29**, 215.

|| For equilibria, see B. Topley and H. Eyring, *J. Chem. Phys.* 1934, **2**, 217.

¶ *Nature*, 1933, **132**, 892.

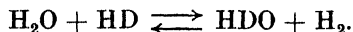
†† E. Fajans, *Z. physikal. Chem.* 1935, B **28**, 239.

‡‡ R. Burstein, *Acta Physicochim. U.R.S.S.* 1938, **8**, 857.

§§ J. Horiuti and M. Polanyi, *Nature*, 1933, **132**, 819.

|||| A. J. Gould and W. Bleakney, *J. Amer. Chem. Soc.* 1934, **56**, 247.

Again, the exchange may also be induced by hydrogen-activating oxides† such as Cr_2O_3 or ZnO ; and work has also been done on the intermediate reaction‡

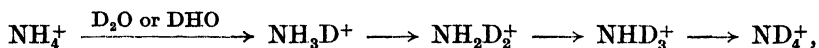


The catalytic deuteration of ammonia has been investigated by Wirtz,§ using platinum, by Taylor and Jungers|| in the presence of an ammonia-synthesis catalyst ($\text{Fe}-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$), and by Farkas,¶ who employed iron. All the possible ammonias are formed, even with iron catalysts at room temperature, and can be recognized by their band spectra.

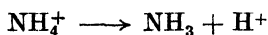
A similar catalytic deuteration of aromatic nuclei also occurs. Thus Horiuti, Ogden, and Polanyi†† found that if benzene is shaken with deuterium at ordinary temperatures in the presence of platinum black, exchange takes place with, under these conditions, very little hydrogenation.

(iii) *Exchange by Ionization in Solutions*

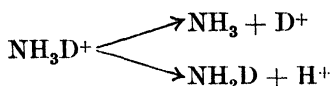
One of the earliest observed reactions of this type‡‡ is the deuteration of solutions of ammonia or ammonium salts in heavy water



in which§§ equilibria such as



or



provide the necessary hydrogen or deuterium ions.

Ionic deuteration also takes place in other cases in which both of the exchanging molecules are of such a nature that appreciable dissociation into products including deuterium or hydrogen ions occurs. Thus, simple mixing of D_2O (or DHO) with water-soluble organic

† H. S. Taylor and H. Diamond, *ibid.* 1935, **57**, 1256.

‡ A. and L. Farkas, *Trans. Faraday Soc.* 1934, **30**, 1071; *J. Chem. Phys.* 1934, **2**, 468; K. F. Bonhoeffer and K. W. Rummel, *Naturwiss.* 1934, **22**, 45.

§ K. Wirtz, *ibid.* 1935, **23**, 721; *Z. physikal. Chem.* 1935, B **30**, 289.

|| H. S. Taylor and J. C. Jungers, *J. Amer. Chem. Soc.* 1935, **57**, 660.

¶ A. Farkas, *Trans. Faraday Soc.* 1936, **32**, 416.

†† J. Horiuti, G. Ogden and M. Polanyi, *ibid.* 1934, **30**, 663.

‡‡ K. F. Bonhoeffer and G. W. Brown, *Z. physikal. Chem.* 1933, B **23**, 171.

§§ See A. Farkas, *Light and Heavy Hydrogen*, p. 199.

bodies containing hydroxyl groups,† such as glycol, phenol, or the sugars, or with substances containing —SH or —NH₂ groups, is sufficient to cause exchange, as is shown by the depression of the deuterium content of the heavy water after this is distilled off. In these reactions it is merely the hydrogen of the hydroxyl, etc., group which reacts. The hydrogen atoms in, for instance, the —CH₂— groups in glycol or in methyl or similar groups do not readily exchange with deuterium ions in solution.

An interesting case of ionic deuteration is to be found in the deuteration of benzene on shaking this with heavy water containing D₂SO₄.‡ By repeating the treatment a sufficient number of times, exhaustive deuteration occurs with production of substantially pure hexadeuterobenzene.§

While all the above reactions involve the substitution of deuterium for hydrogen, the reverse change, i.e. the substitution of hydrogen for deuterium, also occurs, subject to equilibrium conditions.

PROPERTIES OF DEUTERIUM COMPOUNDS

Heavy Water

This is treated in greater detail than other deuterium compounds on account of its importance. Some physical properties of pure D₂O, compared with those of ordinary water, are summarized in Table 38.

TABLE 38

	D ₂ O	H ₂ O
Triple point, ° C.	3.8	0
Boiling-point, ° C.	101.42	100
Temp. of max. density, ° C.	11.6	4
Critical temperature, ° C.	371.5	374
Critical pressure, atm.	218.6	217.7
Sp. gr. of ice at m.p.	1.017	0.917
Density of water at 25°	1.1056	1.0000
Molecular lowering of f. pt.	2.050°	1.859°
Surface tension, dynes/cm. at 19°	72.83	72.66
n_D^{20} (liquid)	1.3284	1.3330

† N. F. Hall, E. Bowden, and T. O. Jones, *J. Amer. Chem. Soc.* 1934, **56**, 750; Bonhoeffer and Brown, loc. cit.; see also C. K. Ingold and C. L. Wilson, *Z. Elektrochem.* 1938, **44**, 62.

‡ C. K. Ingold, G. G. Raisin, and C. L. Wilson, *Nature*, 1934, **134**, 734.

§ C. K. Ingold, G. G. Raisin, and C. L. Wilson, *J. Chem. Soc.* 1936, 916.

Some of the physical properties of two other waters, namely, the intermediate water, HDO, and water containing the heavy oxygen isotope, ^{18}O , have been measured by Riesenfeld and Chang.† These are given below:

TABLE 39

	H_2^{16}O (ordinary water)	HD^{16}O	H_2^{18}O
Boiling-point, ° C.	100.00	101.76	100.13
Vapour pressure at 20°, mm. . . .	17.535	16.27	17.37
Vapour pressure at 100°	760.0	739.71	756.50
Latent heat of vaporization at boiling- point, cal./mole	9,719	9,849	9,732

Specific Gravity and Molecular Volume. The molecular volume of liquid D_2O at various temperatures (from which the specific gravity can readily be obtained by the relationship: $\text{sp. gr.} = \frac{\text{mol. wt.}}{\text{molec. volume}}$) has been determined by a number of workers including Bridgman,‡ who also measured the compressibility, Taylor and Sherman,§ and Lewis and Macdonald.|| Bridgman's results are contained in Table 40.

TABLE 40

Temperature, ° C.	Molecular volume	
	D_2O	H_2O
10	18.122	18.018
20	18.125	18.048
40	18.200	18.157
50	18.270	18.233
60	18.363	18.323
80	18.570	18.539
100	—	18.800

The uneven expansion with rise in temperature, with passage, at 11.6°, through a state of maximum density (minimum volume) is more clearly seen from the figures of Lewis and Macdonald in

† E. H. Riesenfeld and T. L. Chang, *Z. physikal. Chem.* 1936, B 33, 132.

‡ P. W. Bridgman, *J. Chem. Phys.* 1935, 3, 597.

§ H. S. Taylor and P. W. Sherman, *J. Amer. Chem. Soc.* 1934, 56, 998.

|| G. N. Lewis and R. T. Macdonald, *ibid.* 1933, 55, 3057.

which the volume at t° is expressed as a fraction of the volume at 4° .

TABLE 41

Temperature, $^\circ\text{C.}$	$\frac{\text{Molec. vol. D}_2\text{O at } t^\circ}{\text{Molec. vol. D}_2\text{O at } 4^\circ}$
5	0.99987
10	0.99948
15	0.99958
20	1.00016
30	1.00243
40	1.00605

Density of Mixtures of D_2O and H_2O . The density of mixtures of heavy and light water is of considerable practical importance, since it forms a widely used method of assessment of the heavy water content. The variation is nearly, but not quite, linear with the molecular fraction of D_2O present.†

If x is the molecular fraction of D_2O in the sample and Δs is the difference in density, at 25° , between the sample and ordinary water,

$$x = 9.579\Delta s - 1.03(\Delta s)^2,$$

or, less accurately, if the variation is taken as linear,

$$\Delta s = 0.1056x.$$

In the above relationships, which are due to Lewis and Luten, Lewis and Macdonald's value, $d_{25}^{25} = 1.1056$ (or $\Delta s = 0.1056$), is assumed for pure D_2O .

Alternative Method of Analysis by Refractive Index. Lewis and Luten state that the refractive index of a D_2O — H_2O mixture varies linearly with the molecular fraction and give the following relationship, in which Δn is the difference, at 25° , between the refractive index of the sample to be analysed and that of ordinary water. If x is the molecular fraction of D_2O , as before,

$$\Delta n = -0.00449x \text{ (for white light)}$$

or $\Delta n = -0.00445x$ (for the sodium D -line).

The refractive index method is both rapid and accurate; and, by combining this with the density method given in the preceding section, the amount of H_2^{18}O present may also be estimated. Using

† G. N. Lewis and D. B. Luten, *J. Amer. Chem. Soc.* 1933, **55**, 5061; D. B. Luten, *Phys. Rev.* 1934, **45**, 161.

the same nomenclature as before, if y is the molecular fraction of H_2^{18}O and x that of D_2O (in excess of their values in normal water), we have

$$x = 1.370\Delta s - 190.5\Delta n$$

$$y = 7.692\Delta s + 180.9\Delta n.$$

Vapour Pressure. The vapour pressure of solid D_2O is given by Bartholomé and Clusius† as 3.65 mm. at 0° or 5.06 mm. at the triple point. The vapour pressure of ordinary ice at 0° is 4.58 mm.

The vapour pressure, in millimetres, of liquid D_2O is as follows.‡ The values for ordinary water are taken from the *International Critical Tables*.

TABLE 42

$t, ^\circ \text{C.}$	$P_{\text{H}_2\text{O}} - P_{\text{D}_2\text{O}}$	$P_{\text{H}_2\text{O}}$	$P_{\text{D}_2\text{O}}$
20	2.3	17.5	15.2
30	3.9	31.8	27.9
40	6.1	55.3	49.2
50	9.1	92.5	83.4
60	13.1	149.4	136.3
70	18.0	233.7	215.7
80	23.9	255.1	231.2
90	30.7	525.8	495.1
100	38.4	760.0	721.6
110	47.0	1,074.6	1,027.6

Vapour pressures have also been determined by Topley and Eyring§ (whose values at 100° and 110° differ somewhat from those of Lewis and Macdonald) and by Riesenfeld and Chang.|| The latter authors measured vapour pressures at higher temperatures and point out that, since the critical temperature of D_2O is lower than that of H_2O ,¶ the vapour-pressure curve of D_2O should cut that of H_2O at a temperature slightly above 200° . It will be seen from Riesenfeld and Chang's experimental results at these higher temperatures, reproduced in Table 43, that the actual point of intersection is about 225° and that, above this, the vapour pressure of D_2O is, as expected, higher than that of H_2O .

† E. Bartholomé and K. Clusius, *Z. physikal. Chem.* 1935, B **28**, 167.

‡ G. N. Lewis and R. T. Macdonald, *J. Amer. Chem. Soc.* 1933, **55**, 3057.

§ B. Topley and H. Eyring, *J. Chem. Phys.* 1934, **2**, 217.

|| E. H. Riesenfeld and T. L. Chang, *Z. physikal. Chem.* 1936, B **33**, 120.

¶ E. H. Riesenfeld and T. L. Chang, *ibid.* 1935, B **28**, 167.

TABLE 43

Temperature, ° C.	Vapour pressure, atm.	
	H ₂ O	D ₂ O
100	1.0000	0.9503
150	4.6982	4.5966
200	15.341	15.260
225	25.151	25.151
230	27.591	27.615
371.5	211.615	218.6
(Crit. temp. of D ₂ O)		

Latent and Specific Heats. Some values for various latent heats, in kg.-cals. per mole, due to Bartholomé and Clusius,† are contained in Table 44.

TABLE 44

	D ₂ O	H ₂ O
Latent heat of fusion at m.p. . .	1.522	1.435
Latent heat of sublimation at m.p. .	12.631	12.170
Latent heat of vaporization at m.p. .	11.109	10.735

The variation of the latent heat of vaporization of liquid D₂O with the temperature, as calculated by Riesenfeld and Chang from their vapour-pressure curves, is as follows:

TABLE 45

Temperature, ° C.	Latent heat, in kg.-cals. per mole	
	D ₂ O	H ₂ O
10	11.005	10.645
20	10.875	10.550
30	10.753	10.453
50	10.517	10.255
100	9.919	9.719

The molecular heat of liquid D₂O at various temperatures has been measured by Brown, Barnes, and Maas,‡ whose results are summarized in Table 46.

If these values are reduced to calories per gram, in place of calories per mole, the specific heat of D₂O is not greatly different from that of water. It may, however, be noted that Bartholomé and Clusius§ give a value of 18.18 g.-cals. for the molecular heat at 18° C.

† E. Bartholomé and K. Clusius, *Z. physikal. Chem.* 1935, B 28, 167.

‡ R. S. Brown, W. H. Barnes, and O. Maas, *Canad. J. Res.* 1935, 12, 699; 13, 167.

§ E. Bartholomé and K. Clusius, *Z. physikal. Chem.* 1935, B 28, 174.

TABLE 46

Temperature, ° K.	C_p of D_2O in g.-cals.	Ratio $\frac{C_p \text{ of } D_2O}{C_p \text{ of } H_2O}$
280	20.15	1.115
290	19.91	—
295	19.78	1.110

DEUTERATES

Like ordinary water, D_2O may be associated with salts and other compounds as water of crystallization. A number of these hydrates has been studied,† for instance, $CuSO_4 \cdot 5D_2O$, $Na_2SO_4 \cdot 10D_2O$, $MgSO_4 \cdot 7D_2O$, $NiCl_2 \cdot 6D_2O$, and $CoCl_2 \cdot 6D_2O$.

In general, the vapour tension of deuterates is slightly less than that of the corresponding hydrate at the same temperature. Figures for $CuSO_4 \cdot 5D_2O$, $SrCl_2 \cdot 6D_2O$, and $NaBr \cdot 2D_2O$ are given in Table 47.

TABLE 47

Temp., ° C.	Vapour tensions, in mm. Hg				
	$CuSO_4$	$SrCl_2$		$NaBr$	
	$5D_2O$	$6D_2O$	$6H_2O$	$2D_2O$	$2H_2O$
25	6.655	6.9	7.3	6.9	7.5
30	9.285	10.7	11.0	10.45	11.3
40	—	20.4	22.0	21.6	22.9

The heat of hydration is usually less for the deuterates than for the hydrates: thus Partington calculated a heat of combination of 2,219 g.-cals. per molecule of D_2O for $CuSO_4 \cdot 5D_2O$ compared with a corresponding heat of 2,780 cal. for $CuSO_4 \cdot 5H_2O$, assuming that the change in hydration (probably from $CuSO_4 \cdot 5H_2O$ to $CuSO_4 \cdot 3H_2O$) was the same for the hydrate and the deuterate at the temperature of the measurements.

This similarity between D_2O and H_2O persists even in the formation of unstable deuterates such as $Kr \cdot 6D_2O$ and $Xe \cdot 6D_2O$, corresponding‡ with the hydrates $Kr \cdot 6H_2O$ and $Xe \cdot 6H_2O$.

OTHER DEUTERIUM COMPOUNDS

It has been possible to treat heavy water in considerable detail on account of the large amount of work which has been done on it.

† J. Bell, *J. Chem. Soc.* 1937, 459; J. R. Partington and K. Stratton, *Nature*, 1936, 137, 1075.

‡ M. Godechot, G. Cauquil, and R. Calas, *Compt. rend.* 1936, 202, 759.

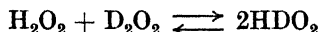
A number of other deuterium compounds of various types has now also been prepared, either by exchange or by special reactions involving no light hydrogen; but the published material at present available with respect to the preparation and properties of inorganic deuterium compounds is not sufficient to make possible a systematic description of compounds with various elements in the order of the periodic system. For this reason, the other compounds will be arranged in the following order: other compounds with oxygen (including metallic deuteriooxides), sulphides and selenides, halides and other deuterio-acids, deuterio-ammonias including the corresponding phosphines and arsines, and various deuterium compounds, with which it will be convenient to include deuterio-methane and deuterio-benzene, although these are not inorganic compounds.

Deuterium Peroxide, D₂O₂

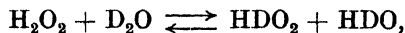
This can obviously be prepared by methods analogous to those used for H₂O₂, e.g. by the action of barium peroxide on dilute deuterio-sulphuric acid (D₂SO₄ in D₂O). Its preparation in a pure state by a cyclic method in which excessive use of D₂O is avoided has been described by Fehrer.† In this process heavy water vapour is passed, in an all-glass apparatus, through a mixture of D₂SO₄ and potassium persulphate at 70–90°. The resulting mixture of D₂O and D₂O₂ vapour is condensed and fractionated, the fractions less rich in peroxide being re-cycled through the oxidizing mixture until substantially complete conversion to the peroxide is obtained. The heavy sulphuric acid was made by the direct union of D₂O with sulphur trioxide.

The density, at 18°, of pure D₂O₂ is given as 1.529, compared with 1.4649 for pure H₂O₂; and products having a purity up to 99.7 per cent. were obtained.

It may be noted that the mixed deuterium-hydrogen peroxide, HDO₂, is formed by the exchange reactions‡



or



but it has not been prepared in a pure state.

† F. Fehrer, *Ber.* 1939, **72**, 1789; see also H. Pietzsch and G. Adolph, *Ger. Pats.* 241,702, 256,148, and 293,087.

‡ F. Fehrer, *Z. Elektrochem.* 1937, **43**, 663; H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, 1934, **17**, 970; E. Abel, O. Redlich, and W. Stricks, *Monatsh.* 1935, **65**, 380.

Alkali Deuterioxides

Breuer† has prepared sodium deuterioxide, NaOD, by the action of D₂O vapour on metallic sodium. Its solubility in D₂O is stated to be less than that of NaOH in H₂O, but its other properties have not been described.

Deuterium Sulphides and Selenide

The normal deuterium sulphide, D₂S, has been made by A. H. and H. H. Nielsen‡ by the action of D₂O on aluminium sulphide. If the latter substance is present in excess and the entrained heavy water is removed in a trap, the D₂S is obtained in a pure condition. Its properties, together with those of deuterium selenide, which can be prepared in a similar way,§ are summarized in Table 48, these figures being due to Kruis, Popp, and Clusius.||

TABLE 48

	D ₂ S	H ₂ S	D ₂ Se	H ₂ Se
Melting-point, ° Abs.	187.1	187.6	206.2	207.4
Latent heat of fusion, cal./mole	565	568	596	601
Vapour pressure at m.p., mm. Hg	163.0	173.7	193.4	205.4

All these sulphides and selenides are capable of existence in three forms in the solid state with definite transitions, for details of which reference should be made to the paper by Kruis, Popp, and Clusius.

The intermediate sulphide, DHS, was prepared in an impure form by dropping an approximately equimolecular mixture of D₂O and H₂O on aluminium sulphide. It contained some D₂S and H₂S, but the presence of DHS could be recognized by its infra-red absorption spectrum.

Acids containing Deuterium

Acids derived from anhydrides are in many cases readily made by the action of these anhydrides on D₂O, e.g. D₂SO₄ from D₂O and SO₃ or deuterophosphoric acids from P₂O₅ and D₂O.

Of the deuterio-halides, DCl, DBr, and DI have been prepared by a number of methods,¶ for instance, by the direct combination of the

† F. W. Breuer, *J. Amer. Chem. Soc.* 1935, **57**, 2236.

‡ *J. Chem. Phys.* 1936, **4**, 229.

§ O. E. Frevold, O. Hassel, and K. Skjulstad, *Physikal. Z.* 1936, **37**, 134.

|| A. Kruis, L. Popp, and K. Clusius, *Z. Elektrochem.* 1937, **43**, 664.

¶ C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.* 1935, **31**, 1392; L. and

elements, including, for DCl, photochemical synthesis and, for DBr and DI, catalysed interaction in the presence of catalysts such as platinum black. DCl has also been made by reducing silver chloride with deuterium† at 700° or by the action of D₂O on anhydrous magnesium chloride‡ at 600°. Other methods include the treatment of NaCl with D₂SO₄ or the action of D₂O on thionyl chloride or benzoyl chloride.§ Deuterium fluoride, D₂F₂, has been prepared by Clausen and Hildebrand|| by the reduction of silver fluoride with deuterium at 110° in a silver tube.

The melting- and boiling-points of the various halides, as tabulated by Clusius¶ from the results of various authors, are given below:

TABLE 49
Deuterium Halides

<i>Halide</i>	<i>Melting-point,</i> <i>° Abs.</i>	<i>Boiling-point,</i> <i>° Abs.</i>
D ₂ F ₂	—	291·8
H ₂ F ₂	—	293·1
DCl	158·2	191·6
HCl	162·2	188·1
DBr	185·7	206·3
HBr	186·2	206·3
DI	221·5	237·0
HI	222·3	237·5

Among other deutero-acids, the cyanide, DCN, has been prepared by Lewis and Schutz,†† who also measured its vapour-pressure curve. It melts at -12° C. (m.p. of HCN is -14°) and boils at 26·1° (b.p. HCN, 25·5°).

Deuterides of the Ammonia Type

In addition to its formation by exchange, deutero-ammonia, ND₃, may be prepared by processes such as the interaction of D₂O and

A. Farkas, *Naturwiss.* 1934, **22**, 218; D. Rittenberg and H. C. Urey, *J. Amer. Chem. Soc.* 1934, **56**, 1820; J. E. Bates, J. O. Halford, and L. C. Anderson, *J. Chem. Phys.* 1935, **3**, 415, 531.

† H. Steiner and E. K. Rideal, *Proc. Roy. Soc.* 1939, A **173**, 504.

‡ G. N. Lewis, R. T. Macdonald, and P. W. Schutz, *J. Amer. Chem. Soc.* 1934, **56**, 494.

§ O. F. Frevold, O. Hassel, and S. Rustad, *Physikal. Z.* 1937, **38**, 193; A. Langseth and A. Klit, *Kgl. Danske Videnskap. Math. Fys. Medd.* 1937, **15**, No. 13, 4.

|| W. H. Clausen and J. H. Hildebrand, *J. Amer. Chem. Soc.* 1934, **56**, 1820.

¶ K. Clusius, *Z. Elektrochem.* 1938, **44**, 25.

†† G. N. Lewis and P. W. Schutz, *J. Amer. Chem. Soc.* 1934, **56**, 1002.

magnesium nitride.† If the D_2O contains HDO or H_2O , the intermediate molecules, NH_2D and NHD_2 , are also produced.

The triple point of ND_3 is 196.6° Abs., its boiling-point is 242.1° ($NH_3 = 195.3^\circ$ and 239.8°), and its vapour pressure at various temperatures is as follows:

TABLE 50

Temperature, $^\circ$ Abs.	Vapour pressure, mm.	
	ND_3	NH_3
202.3	63	77
213.0	154	184
226.1	313	364
232.1	445	511
238.6	628	714

Its latent heat of vaporization is slightly higher than that of ammonia, i.e. 5,990 g.-cals. per mole compared with 5,797 for NH_3 .

Deuterophosphine, PD_3 , has been made by Barrer‡ by acting on calcium phosphide with heavy water vapour, and deuterioarsine, AsD_3 , by de Hemptinne and Delfosse§ from sodium arsenide and D_2O .

Deutero-Hydrocarbons

Deuteromethane, CD_4 , is most conveniently prepared|| by the action of D_2O on aluminium carbide. It has also been made¶ by the catalytic reduction of carbon dioxide by deuterium, using a nickel catalyst and a reaction temperature of 350° . Some of its physical properties, compared with those of methane, are tabulated below, the figures being those given by Kruis, Popp, and Clusius.††

TABLE 51

	CD_4	CH_4
Melting-point, $^\circ$ Abs.	89.2	90.6
Latent heat of fusion, cal./mole	215.7	224.0
Vapour pressure at triple point, mm.	78.9	87.5

† H. S. Taylor and J. C. Jungers, *ibid.* 1933, **55**, 5057.

‡ R. M. Barrer, *Trans. Faraday Soc.* 1936, **32**, 486, 490.

§ M. de Hemptinne and J. M. Delfosse, *Bull. Acad. Roy. Belge*, 1935, **21**, 793;
J. M. Delfosse, *Nature*, 1936, **137**, 868.

|| Barrer, *loc. cit.*

¶ E. Bartholomé, G. Drikos, and A. Eucken, *Z. physikal. Chem.* 1938, B **39**, 371.

†† A. Kruis, L. Popp, and K. Clusius, *Z. Elektrochem.* 1937, **43**, 664.

Unlike methane, deuteromethane exists in three distinct solid forms, with transition points at 21.4° and 26.3° Abs.

Deutero-benzene has been prepared in a substantially pure state by repeated exchange between D_2O and ordinary benzene either in the liquid phase† in the presence of D_2SO_4 or at 200° on catalysts such as nickel.‡ It has also been made, with a purity up to 98 per cent., by exchange between DCl and benzene catalysed by aluminium chloride.§

The following data (save the melting-point, which is that given by Klit and Langseth) are due to Ingold and his co-workers.||

TABLE 52

	C_6D_6	C_6H_6
Melting-point, $^{\circ}C.$	6.64	5.5
Boiling-point, $^{\circ}C.$	79.288	80.112
d_{25}^{25}	0.94560	0.87596
n_D^{22}	1.49779	1.49882

Its vapour pressure at various temperatures is given in Table 53.

TABLE 53

Temperature, $^{\circ}C.$	Vapour pressure, mm.	
	C_6D_6	C_6H_6
0	27.5	26.5
10	46.9	45.4
20	77.1	74.7
30	121.8	118.2
40	186.3	181.1
50	276.7	269.0
60	399.4	388.6
70	562.0	547.4
80	773.6	753.6

Many other deuterio-hydrocarbons are known. Thus, deutero-naphthalene melts at 77.5° ; but a detailed description of these is omitted for reasons already given.

† C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J. Chem. Soc.* 1936, 915.

‡ P. I. Bowman, W. S. Benedict, and H. S. Taylor, *J. Amer. Chem. Soc.* 1935, 57, 960.

§ A. Klit and A. Langseth, *Z. physikal. Chem.* 1936, A 176, 65.

|| For other determinations of physical properties, see H. Erlenmeyer and H. Lobeck, *Helv. Chim. Acta*, 1935, 18, 1464.

Metallic Deuterides

As would be expected, deuterium forms metallic compounds analogous to the hydrides. Hackspill and Borocco† have described the preparation of deuterides of the alkali metals by circulating deuterium over sodium, potassium, rubidium, or caesium at or below 360°. Lithium deuteride, LiD, has been made similarly.‡ These deuterides closely resemble the hydrides both in their chemical properties and in their crystal structure. The lattice constants of LiD, which like LiH has a rock salt structure, are slightly smaller (about 0.5 per cent.) than those of LiH.

TRITIUM (^3H OR T)

The hydrogen isotope ^3H , in addition to its production by bombardment methods, appears to occur naturally in very small quantities: thus Selwood, Taylor, and Bleakney,§ who obtained evidence for its presence in water (in which it can be concentrated electrolytically), estimate the abundance of tritium in ordinary water to be about 7 parts in 10^{10} ; and it has also been detected in heavy water by Lozier, Smith, and Bleakney.||

In the course of the former work, 75 tons of ordinary water were electrolysed down to 0.5 c.c., when the abundance of tritium, which was estimated mass-spectrographically, rose to 1 part in 10^4 . Mass lines were obtained for hydrogen ions of masses 6, 5, and 4. These could be assigned, on the basis of the variation of their intensity with pressure, to triatomic ($I \propto p^2$) and to diatomic ($I \propto p$) molecules respectively; and it was shown in this way that the ion of mass 6 was probably D_3^+ , the ions of mass 5 consisting of $(\text{DT})^+$ with a trace of $(\text{D}_2\text{H})^+$, while those of mass 4 were probably D_2^+ . There is no mention in this paper of the radioactivity of the tritium thus concentrated.

Preliminary evidence for the production of tritium by the bombardment of targets containing deuterium (ND_4Cl , $(\text{ND}_4)_2\text{SO}_4$, and D_3PO_4) with deuterons was obtained by Oliphant, Harteck, and Rutherford,¶ also by Dee,†† who gives a clear photograph of its mass

† L. Hackspill and A. Borocco, *Compt. rend.* 1937, **204**, 1475.

‡ E. Zintl and A. Harder, *Z. physikal. Chem.* 1935, B **28**, 478.

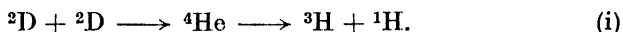
§ P. W. Selwood, H. S. Taylor, W. W. Lazier, and W. Bleakney, *J. Amer. Chem. Soc.* 1935, **57**, 780; see also W. Bleakney and A. J. Gould, *Phys. Rev.* 1934, **45**, 281.

|| W. W. Lozier, P. T. Smith, and W. Bleakney, *ibid.*, p. 655.

¶ M. L. E. Oliphant, P. Harteck, and Lord Rutherford, *Proc. Roy. Soc.* 1934, A **144**, 692.

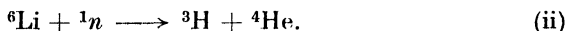
†† P. I. Dee, *Nature*, 1934, **133**, 564.

line. Oliphant, Harteck, and Rutherford consider that a helium atom, in a sufficiently high energetic state to be unstable, is formed as an intermediate product, the complete reaction being represented by



The high energy of the helium intermediate follows from energy-mass considerations, according to which the helium particle has a mass of 4.0272, including its excess energy expressed in mass units. It thus possesses an excess energy of about 23 Mev. over the normal ^4He atom (the mass of which is taken as 4.0022) and is accordingly unstable. A modification of the above production of tritium from deuterium has been described by Harnwell and others,[†] who reported its formation by passing canal rays, produced by a high-voltage discharge in deuterium at a low pressure, into deuterium at a higher pressure.

^3H may also be obtained by the action of slow neutrons on lithium,[‡] the reaction being



In a typical experiment, metallic lithium, sealed in a glass tube, was exposed inside a large paraffin block to neutrons from a 100 mg. Ra—Be source. After an irradiation period of four months, the lithium was treated with water, with production of lithium hydroxide and of hydrogen containing, in over 90 per cent. yield, the radioactive ^3H formed as a result of the neutron bombardment. In other experiments lithium was bombarded with slow neutrons from a cyclotron.

Further reactions in which ^3H is produced include the bombardment§ of boron or nitrogen, in the form of a solution of boric acid or ammonium nitrate, with fast neutrons.

Mass of the ^3H Atom

The mass of the tritium atom may be deduced from the energy-mass data involved in the breaking up of the postulated unstable helium nucleus into a proton and a ^3H nucleus. Oliphant, Harteck, and Rutherford found that the ^1H particle produced along with the ^3H in reaction (i) of the preceding section possessed an energy of 3×10^6 electron-volts: accordingly, from momentum considerations,

[†] G. P. Harnwell, H. D. Smyth, S. N. Voorhis, and J. B. H. Kuper, *Phys. Rev.* 1934, **10**, 655.

[‡] J. Chadwick and M. Goldhaber, *Proc. Camb. Phil. Soc.* 1935, **31**, 612; R. D. O'Neal and M. Goldhaber, *Phys. Rev.* 1940, **58**, 574.

[§] R. Cornog and W. F. Libby, *ibid.* 1941, **59**, 1046.

the energy of the ${}^3\text{H}$ particle, which is emitted in the opposite direction, will be 1×10^6 electron-volts, i.e. the total energy of the two particles is 4×10^6 electron-volts, corresponding with a mass change of 0.0043 units. Hence the mass of the ${}^3\text{H}$ atom will be

$$4.0272 - (1.0078 + 0.0043) \quad \text{or} \quad 3.0151,$$

the values 4.0272 (see previous section) and 1.0078 representing the masses of the helium and of the proton. Chadwick and Goldhaber, on the basis of an energy release of 0.0051 mass units (4.7 Mev.) in equation (ii) of the previous section, calculate a mass of 3.0061 for the ${}^3\text{H}$ atom.

Decay Constant and Half-lifetime of ${}^3\text{H}$

${}^3\text{H}$ is β -active. The β -rays produced in the spontaneous radioactive decay have a relatively low energy, the maximum value for which has been estimated by O'Neal† at 15 ± 3 kev.

Its decay constant, λ , which has the dimensions of reciprocal time (see Chapter VII), is too small to be determined conveniently in the usual way from the decay curve;‡ but it has been evaluated by O'Neal and Goldhaber by producing a known number, N , of ${}^3\text{H}$ nuclei and observing the number, N' , which decay in unit time, the electrons produced during the decay being counted in a Geiger counter and λ being obtained from the relationship $\lambda = N'/N$. As a result of these measurements

$$\lambda = 7 \times 10^{-10} \pm 25 \text{ per cent. reciprocal seconds}$$

or the half-life of ${}^3\text{H} = 31 \pm 8$ years.

† R. D. O'Neal, *Phys. Rev.* 1941, **60**, 359.

‡ R. D. O'Neal and M. Goldhaber, loc. cit.

III

RECENT CHEMISTRY OF THE HALOGENS

PROBABLY the most interesting advance in this field has been the preparation of oxides of fluorine and of bromine, in that these two halogens were the only elements the oxides of which were unknown, except, of course, the inactive gases. In addition, our knowledge of certain other halogen oxides—particularly chlorine hexoxide, Cl_2O_6 , and the oxides of iodine—has been considerably extended. Among other halogen compounds, covalent nitrates such as $\text{F}.\text{NO}_3$ are of special interest: further, much has now been done to clarify the chemistry of the inter-halogen compounds.

PREPARATION OF FLUORINE

The improved technique which has now been developed for the relatively easy production of elementary fluorine has had corresponding consequences in the preparation of fluorine compounds generally and will be treated first.

In Moissan's original work† a platinum or platinum-iridium U-tube, cooled to -23° by immersion in a methyl chloride bath, was used as the electrolysis chamber, the electrolyte being anhydrous hydrofluoric acid containing some (e.g. 20 per cent.) $\text{HF}.\text{KF}$.

In later work by various investigators it has been found more convenient to electrolyse a fused salt (usually $\text{HF}.\text{KF}$, m.p. 227°), even though this involves the use of a relatively high temperature, since, under these conditions, metals other than platinum can be used: further, most of the more modern electrolytic cells are cylindrical in form, consisting of concentric electrodes separated by a perforated metallic diaphragm, the external pot being used as the cathode. As material for the vessel, copper,‡ nickel,§ monel metal,|| or even magnesium¶ has been used. The anode is usually of graphite. Efforts have been made to reduce the melting-point of the electrolyte, without giving up the advantage of being able to use the above constructional materials, by employing melts containing a ratio of

† H. Moissan, *Ann. Chim. Phys.* (6), 1887, **12**, 473; 1891, **24**, 226.

‡ W. L. Argo, F. C. Mathers, B. Humiston, and C. O. Anderson, *J. Phys. Chem.* 1919, **23**, 348.

§ W. T. Miller and L. A. Bigelow, *J. Amer. Chem. Soc.* 1936, **58**, 1585.

|| W. C. Schumb and E. L. Gamble, *ibid.* 1930, **52**, 4302.

¶ N. C. Jones, *J. Phys. Chem.* 1929, **33**, 811.

HF to KF higher than unity. Thus, $\text{KF} \cdot 3\text{HF}$, which seems to be a definite compound and melts at 56° (electrolysis temperature 56 – 150°), has been recommended by Lebeau and Damiens;[†] or the proportion of HF has been raised arbitrarily, for instance,[‡] to a HF:KF ratio of 1.6, by leading gaseous HF into the HF.KF melt, the electrolysis being carried out at 160° . Acid caesium fluoride ($\text{CsF} \cdot 2\text{HF}$, m.p. 19°) has also been proposed.[§] With some of these low-melting electrolytes, copper or nickel can apparently be used even for the anode. It may be noted that, with a graphite anode, the fluorine always contains a little carbon tetrafluoride. This, however, can readily be removed by passing the resulting fluorine through a trap cooled in liquid oxygen (b.p. of fluorine = -187°). In any case it is of great importance that the electrolyte should be thoroughly dried before use, since the presence of traces of moisture leads to the presence of oxygen or of fluorine monoxide in the fluorine evolved. The preliminary drying of HF.KF may be carried out in a current of air at 140 – 150° . Argo and his co-workers recommend the replacement of HF.KF by the corresponding sodium salt which is not hygroscopic; but this does not seem to have come into general use.

Some of the difficulties which occur in the safe preparation of fluorine by fused salt electrolysis have been reviewed by Denbigh and Whytlaw-Gray.|| In addition to difficulties inherent in attacks on the material of the cell, foaming or volatilization of the fluoride may cause a blockage in the fluorine exit tube resulting in an explosion due to the mixing of the fluorine and hydrogen: further, the fused electrolyte may creep over the edge of the cell. Other disadvantages of some of the cells which have been described in the literature include a low current efficiency (e.g. 30 per cent.) and the necessity for waiting some time after starting the electrolysis before pure fluorine begins to be evolved.

The apparatus recommended by Denbigh and Whytlaw-Gray is shown in Fig. 17. It consists of a spun copper vessel, A, 9 inches deep, 5 inches in diameter, and $\frac{1}{8}$ inch thick, wound for electrical heating and provided with a flanged cover and an external gully to minimize creeping and, especially, to prevent the fouling of the

[†] P. Lebeau and A. Damiens, *Compt. rend.* 1925, **181**, 917.

[‡] H. Fredenhagen and O. T. Krefft, *Z. Elektrochem.* 1929, **35**, 670.

[§] F. C. Mathers and P. T. Stroup, *Trans. Electrochem. Soc.* 1934, **66**, 113.

|| K. G. Denbigh and R. Whytlaw-Gray, *J. Soc. Chem. Ind.* 1934, **53**, 139 τ .

winding with electrolyte. It is advisable to employ a seamless cell, since the above authors found that a cell with a welded seam was liable to be split on cooling. The diaphragm vessel, *B*, which keeps the fluorine and hydrogen apart, was $11\frac{1}{2}$ inches high and $2\frac{3}{4}$ inches in diameter. It was closed at the bottom to prevent hydrogen rising into the fluorine and was perforated laterally by a number of holes below the level of the electrolyte. The fluorine exit tube, *C*, was of 1-inch copper tubing, this great width effectively preventing blocking

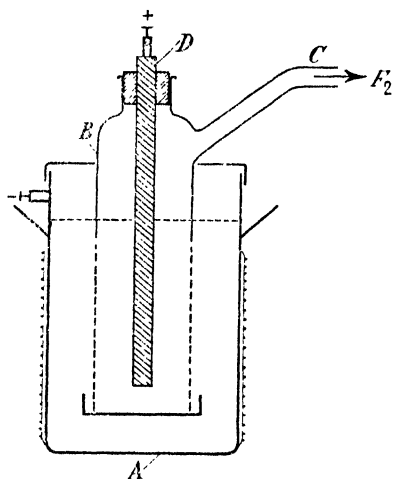


FIG. 17.

up. In a cell with a smaller exit tube Denbigh and Whytlaw-Gray report the occurrence of an explosion due to blockage. The anode, *D*, consisted of a pure Acheson graphite rod, 1 inch in diameter and 11 inches long, cemented into and insulated from the diaphragm collar, as shown, by a thick paste of calcium fluoride and water glass. If this paste is rich in calcium fluoride it is not attacked.

In using the cell, the HF.KF was first thoroughly dried for two days at 140° . A current of 12–15 amperes was required for the electrolysis, the potential difference across the cell being about 13 volts. The cell should be run at a temperature about 10° higher than the melting-point of the electrolyte: a higher temperature leads to the evolution of HF . The current efficiency was of the order of 80 per cent. No blockage and little corrosion was observed.

The above apparatus has been described in detail, since it is typical of the many cylindrical cells which have been employed with various molten electrolytes. Miller and Bigelow,[†] who also discuss the literature, recommend a closed system in order to keep air and moisture from the electrolyte, and employ a U-shaped vessel of cast nickel with graphite electrodes, a detailed drawing of their apparatus being given in their paper. With this cell, a current efficiency up to 89 per cent. was obtained, the fluorine having a purity up to 99 per cent.

[†] Loc. cit.

OXIDES OF FLUORINE

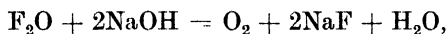
Fluorine Monoxide, F₂O

This was first noticed by Lebeau and Damienst† as a gas accompanying, but distinct from, elementary fluorine derived from the electrolysis of acid potassium fluoride containing a little water. Its formation was most pronounced in the early stages of the electrolysis, and concentrations up to 30 per cent. in the exit gas were obtained under favourable conditions. It differed from fluorine by being less reactive, and from ozone (which Lebeau and Damiens regarded as being a possible product of the reaction) by being colourless in the liquid state. Its reactions with alkalis, whereby an equal volume of oxygen was evolved, and with potassium iodide were studied quantitatively and were used both to establish its composition and as an analytical method for determining the percentage of F₂O in the mixtures obtained.

In a later paper Lebeau and Damienst‡ described a more convenient method of preparation involving the bubbling of elementary fluorine through a dilute solution of sodium hydroxide, the reaction being



Since an excessive time of contact between F₂O and the alkali leads to the destruction of the oxide according to the equation



special conditions are necessary if high concentrations of F₂O are to be obtained. Lebeau and Damiens recommend the passage of fluorine, at the rate of about one litre an hour, through a platinum tube 2 mm. in diameter dipping 1 cm. into a 2 per cent. soda solution. Under these conditions concentrations up to 70 per cent. were obtained directly. The gas leaving the bubbler was collected by the above workers in a receiver containing copper, which removes any accompanying fluorine: it was then liquefied in a liquid air trap and subsequently fractionated.

According to Ruff and Menzel§ it does not attack glass at low temperatures; and operations such as fractional distillation and recondensation can be carried out in glass apparatus, provided that access of air, and consequently of moisture, is avoided by using a

† P. Lebeau and A. Damiens, *Compt. rend.* 1927, **185**, 652.

‡ P. Lebeau and A. Damiens, *ibid.* 1929, **188**, 1253.

§ O. Ruff and W. Menzel, *Z. anorg. Chem.* 1931, **198**, 39.

closed system. Mercury pumps cannot be employed since it attacks mercury; but water-fed filter pumps have been used. It can be adsorbed on active charcoal at low temperatures; and this is probably the most convenient method of pumping off F_2O vapour during distillation. The adsorption is accompanied by a considerable heat effect and must be carried out slowly otherwise an explosion may occur. There is apparently no danger of explosion as a result of the distillation itself. The gas is, however, poisonous, and all exit gases likely to contain F_2O should be passed through traps containing alkaline potassium iodide.

Properties of F_2O

Fluorine monoxide melts at -223.8° and boils at -144.8° . Its critical temperature is about -81° . Its density in the liquid state is 1.90 at the melting-point and 1.54 at the boiling-point.

The vapour pressure, according to Ruff and Menzel (from whose measurements the above constants also are taken), is as follows:

TABLE 54

<i>Temperature,</i> ° C.	<i>Vapour pressure,</i> mm.
—192.2	1.6
—181.9	10.9
—171.3	50.4
—160.4	180.4
—151.2	439.5
—146.1	680.9
—145.2	733.1
—144.8	760.0

Ruff and Menzel† give the heat of formation of F_2O as -7 ± 2 kg.-cals. per mole.

The O—F bond distance and the bond angle, which have been determined by Sutton and Brockway‡ on the basis of electron diffraction data, are 1.4 ± 0.1 Å and $105 \pm 5^\circ$ respectively. Borsch§ obtained the value $100 \pm 3^\circ$. These values for the oxygen bond angle, although not very accurately known for F_2O , should be compared with that in water (105°) and in chlorine monoxide ($111 \pm 2^\circ$), the angle being, as Sutton and Brockway point out, increased above its value in the

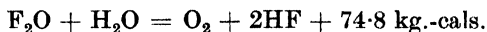
† O. Ruff and W. Menzel, *Z. anorg. Chem.* 1931, **197**, 375; see also H. v. Wartenberg and H. Klinkott, *ibid.* 1930, **193**, 409.

‡ L. E. Sutton and L. O. Brockway, *J. Amer. Chem. Soc.* 1935, **57**, 473.

§ H. Borsch, *Monatsh.* 1935, **65**, 311.

water molecule if heavy groups are bonded to the oxygen. The bond distances, calculated from the radius-sum, should be 1.30 for F_2O and 1.65 for Cl_2O .

Fluorine monoxide is not quickly attacked by cold water, 100 c.c. of which dissolve 6.8 c.c. of F_2O at atmospheric pressure; but the reaction:



occurs explosively on sparking moist F_2O . Its reactions with alkalis have already been described in connexion with its preparation. It should be noted that it differs from Cl_2O in this reaction with alkalis and in the nature of its solution in water by showing little or no tendency to behave as an anhydride of hypofluorous acid: indeed, Lebeau and Damiens, in their first paper, describe it as being 'plutôt un oxyde qu'un anhydride'.

It is completely absorbed by the alkali metals at 400° , with incandescence, and the reaction may be used to determine the fluorine content of the oxide quantitatively. Most other metals also react with the gas, in some cases explosively. A mild explosion was also observed on warming a mixture of F_2O with chlorine, bromine, or iodine. Dry hydrogen does not react at room temperature; but, on sparking, an explosion occurs. With hydrogen sulphide, however, an explosion took place on simple contact. For other chemical properties, reference should be made to Ruff and Menzel's paper.

F_2O_2

This oxide has been prepared by the action of a glow discharge on a mixture of fluorine and oxygen at a low temperature and pressure.† The apparatus used by Ruff and Menzel is shown in Fig. 18. It consisted of a silica discharge-tube with electrodes, *A* and *B*, sealed in with picein joints, the discharge distance being about 12 cm. This tube was cooled by partial or complete immersion in liquid air. The gaseous fluorine and oxygen, obtained from reservoirs of liquid fluorine and oxygen stored at the temperature of liquid air, were led in at the top, as shown, the flow of fluorine being regulated by a valve made of silver or copper and that of the oxygen by an ordinary tap. The outlet of the discharge-tube was connected to a filter-pump and the pressure in the apparatus was adjusted to 15–20 mm., the fluorine-oxygen mixture being allowed to stream through the tube

† O. Ruff and W. Menzel, *Z. anorg. Chem.* 1933, **211**, 204.

continuously at this pressure. An orange solid, melting at about -160° to a red liquid and consisting of F_2O_2 , was deposited on the cooled parts of the apparatus. It was found that a discharge from a large induction-coil, fitted with a Wehnelt interruptor, was more effective than current from a laboratory transformer connected to the alternating current mains and that this led to the complete elimination of oxygen from the fluorine-oxygen mixture used.

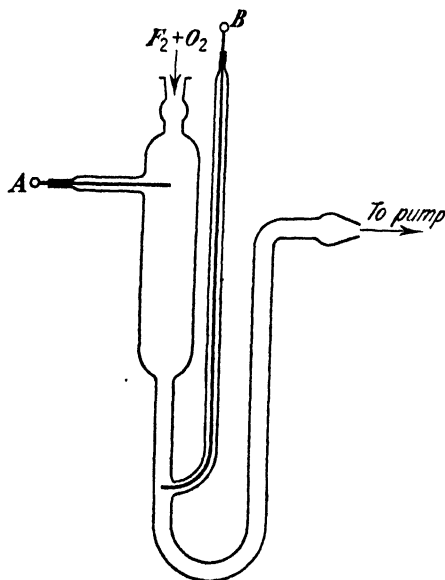


FIG. 18.

The oxide may be vaporized and fractionated without appreciable decomposition at temperatures below -100° and has a vapour density and composition corresponding with F_2O_2 . In the gaseous state F_2O_2 is pale brown, becoming colourless at higher temperatures. Ruff and Menzel first of all regarded this colour-change as involving a transition of F_2O_2 into FO ; but it was subsequently found[†] that the process leads to a mixture of fluorine and oxygen, which would have the same density as that of the supposed FO . In a later publication Ruff[‡] agrees with this and states that the colourless gas, when liquefied, behaves as a mixture of fluorine and oxygen.

[†] P. Frisch and H. J. Schumacher, *Z. anorg. Chem.* 1936, **229**, 423; *Z. physikal. Chem.* 1936, B **34**, 322.

[‡] O. Ruff, *Ber.* 1936, A **34**, 191.

Pure F_2O_2 melts at -163.5° . The determination of its boiling-point and of its vapour-pressure curve above about -95° is complicated by its decomposition; but Ruff and Menzel† give the following figures for the vapour pressure, from which a temperature of about -57° for the boiling-point is obtained by extrapolation.

TABLE 55

Temperature, ° C.	Vapour pressure, mm.
-132	3
-115	15.5
-101	49
-95.5	81
-90	121
-69	555

Its density in the liquid state is given in Table 56.

TABLE 56

Temperature, ° C.	Density
-156	1.734
-141	1.692
-97	1.562
-87	1.533

For its absorption spectrum, reference should be made to the measurements of Brodersen, Frisch, and Schumacher.‡

OXIDES OF CHLORINE

Of the four oxides of chlorine— Cl_2O , ClO_2 , Cl_2O_6 (ClO_3), and Cl_2O_7 —all except the hexoxide have long been known. Cl_2O_6 , including its dissociated form, ClO_3 , possesses a special interest since, although it was probably prepared photochemically by Millon§ as long ago as in 1843, its existence has only recently been clearly established.

Chlorine Hexoxide, $Cl_2O_6 \rightleftharpoons ClO_3$

Millon obtained what was almost certainly chlorine hexoxide by the action of sunlight on ClO_2 at temperatures below 20° . More

† O. Ruff and W. Menzel, *Z. anorg. Chem.* 1934, **217**, 85.

‡ P. H. Brodersen, P. Frisch, and H. J. Schumacher, *Z. physikal. Chem.* 1937, **B 37**, 25.

§ N. A. E. Millon, *Ann.* 1843, **45**, 281.

recently, the formation of a red liquid by the irradiation of chlorine dioxide has been described by Bowen and Booth.†

The subject was further investigated by Bodenstein, Harteck, and Padelt,‡ who prepared the oxide in a pure state and determined its composition. The apparatus used by these workers consisted of an annular glass reaction chamber, immersed in a thermostat at 8–9° and illuminated internally. Tap-grease must be avoided on account of the danger of explosion; and for this reason all valves were of a diaphragm type. Pure ClO_2 was introduced until the pressure was about 500 mm.; and, on switching on the lamp, the walls of the reaction vessel became covered with dark red drops which coalesced to an almost black liquid. The pressure decreased during the irradiation (for instance, from 510 to 355 mm. in 200 min.), showing that the main reaction was one of condensation rather than a decomposition. Since the red liquid was far less volatile than ClO_2 or other oxides of chlorine, it could readily be separated from these by fractionation; and it was obtained in a pure condition by distillation into small U-tubes sealed on to the reaction vessel. Its vapour pressure was about 1 mm. at room temperature.

Its composition was determined by allowing a known small quantity to decompose in an initially evacuated larger vessel maintained first at room temperature and subsequently at a higher temperature for several days, the oxygen being estimated by measuring its volume and the chlorine by interaction with iodide, followed by the titration with thiosulphate of the iodine liberated. The oxygen:chlorine ratio was shown to be almost exactly 3 : 1, corresponding with a formula $(\text{ClO}_3)_n$. Its molecular weight was then measured by the depression of the freezing-point of carbon tetrachloride: this gave a value approximating to Cl_2O_6 .

Chlorine hexoxide can also be prepared by the action of ozone on chlorine dioxide. This method was investigated in a preliminary way by Bodenstein, Harteck, and Padelt and, in greater detail, by Schumacher and Steiger§ and by Goodeve and Richardson.|| In the work of Schumacher and Steiger, dilute ClO_2 prepared by the action of sulphuric acid on a mixture of potassium chlorate and oxalic acid

† E. J. Bowen, *J. Chem. Soc.* 1923, **123**, 2328; H. Booth and E. J. Bowen, *ibid.* 1925, **127**, 510.

‡ M. Bodenstein, P. Harteck, and E. Padelt, *Z. anorg. Chem.* 1925, **147**, 233.

§ H. J. Schumacher and G. Steiger, *Z. anorg. Chem.* 1929, **184**, 272.

|| C. F. Goodeve and F. D. Richardson, *J. Chem. Soc.* 1937, 294.

(which gives a regular stream of ClO_2 diluted with CO_2) was passed, together with ozonized oxygen (c. 8 per cent. O_3), into a reaction vessel of the shape shown in Fig. 19. This vessel was cooled to 0° by means of ice. A suitable ratio is stated to be 1–2 litres per hour of the dilute ClO_2 to about twice this volume of the ozonized oxygen. Goodeve and Richardson's apparatus and method were very similar, save that the reaction temperature was 6° and no CO_2 was used to dilute the ClO_2 . The preparation did not lead directly to a pure product, chlorine dioxide and heptoxide being also present; and the hexoxide was therefore purified by fractional distillation.

Chlorine hexoxide has a melting-point of $3.50 \pm 0.05^\circ$; but it begins to decompose into chlorine dioxide and oxygen even at this temperature: consequently the apparent melting-point of a sample falls with keeping. The latent heats of sublimation and vaporization are given as 12.3 ± 0.5 and 9.5 ± 1 kg.-cals. per mole respectively.

The measurement of its vapour pressure is complicated by its decomposition and, in some circumstances, by its attack on glass; but Goodeve and Richardson give, for the solid:

$$\log_{10} p = -2690/T + 9.3,$$

and, for the liquid:

$$\log_{10} p = -2070/T + 7.1,$$

in which p is the vapour pressure in mm.

Its colour, as well as its melting-point, is readily affected by the presence of impurities. It was originally described as a red liquid; but Goodeve and Richardson state that it is pale yellow at -180° and bright orange-red at -78° .

Some of the physical properties of chlorine hexoxide are compared with those of the other oxides in Table 57, which is taken from Goodeve and Richardson's paper.

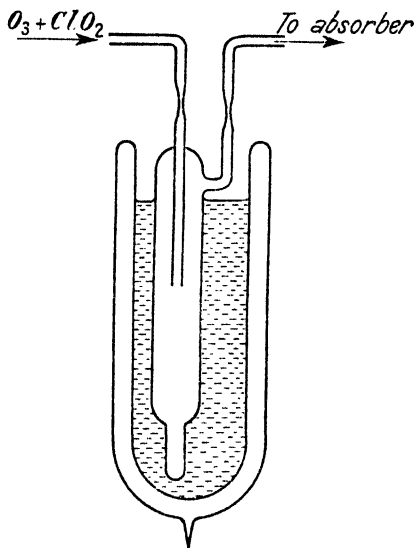
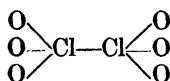


FIG. 19.

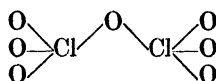
TABLE 57

	Cl ₂ O	ClO ₂	Cl ₂ O ₆	Cl ₂ O ₇
Molecular weight . . .	87	67.5	167	183
Melting-point, ° C. . .	-116	-59	+3.5	-91.5
Boiling-point, ° C. . .	2	11.0	203 (calc.)	80
Latent heat of vaporization	6.20	6.52	9.5	8.29
Vapour pressure, mm. at 0°	699	490	0.31	23.7
Density	—	1.64 at 0°	2.02 at 3.5°	1.86 at 0°

The above authors point out that this oxide has the highest melting-point, the highest density, the highest latent heat of evaporation, and the lowest vapour pressure at a given temperature (corresponding with the highest boiling-point) of all the oxides of chlorine, the difference being especially striking when compared with the heptoxide. This may correspond with a symmetrical structure for the hexoxide, compared with a structure involving an oxygen link for the heptoxide:



(Non-planar)



(Non-planar)

Molecules of the first of these types could pack closer together and thus would be expected to have a higher latent heat of evaporation, and consequently also a higher density and melting-point, than those of the second type. This relationship is parallel with that, for instance, between the aliphatic alcohols and the ethers, which latter have an oxygen link.

Thermal Dissociation of Cl₂O₆ into ClO₃

As has already been mentioned, Bodenstein, Harteck, and Padelt found by cryoscopic measurement that chlorine hexoxide in carbon tetrachloride solution was principally in the form Cl₂O₆. Its molecular complexity in the liquid state at various temperatures has been studied in greater detail by Farquarson, Goodeve, and Richardson,† who have shown that small concentrations of ClO₃ are also present. As a gas, it exists almost entirely‡ as ClO₃.

The method used by Farquarson, Goodeve, and Richardson for measuring the ClO₃ content of liquid Cl₂O₆ is of considerable interest,

† J. Farquarson, C. F. Goodeve, and F. D. Richardson, *Trans. Faraday Soc.* 1936, **32**, 790.

‡ C. F. Goodeve and F. A. Todd, *Nature*, 1933, **132**, 514.

since it gives a further example of the use of magnetic criteria in the determination of structure. Since ClO_3 contains an odd number (41) of circumnuclear electrons, it must contain at least one unpaired electron and will therefore be paramagnetic. The dimer, Cl_2O_6 , on the other hand, which contains an even number of electrons, would be expected to be diamagnetic, provided that, as is probably the case, it is in a $^1\Sigma$ state, with completely balanced electronic spins.

The molar magnetic susceptibilities of ClO_3 and of Cl_2O_6 (which are of opposite signs) can each be calculated, the latter additively, by adding the experimental atomic values, and, in the case of ClO_3 , by means of Van Vleck's relationship:†

$$\chi_{\text{mol.}} = \frac{4N\beta^2 S(S+1)}{3KT} + N\alpha,$$

in which N is the Avogadro number, β is the Bohr magneton (0.9174×10^{-20} e.m.u.), S is the spin quantum number (equal to $\frac{1}{2}$, since all electrons save the odd one are assumed to be paired), K is the Boltzmann constant, and $N\alpha$ is a small residual term, due to high frequency elements, which can be neglected.

On measuring the magnetic susceptibility of liquid chlorine hexoxide experimentally at various temperatures, it was found that the diamagnetism of the mixture was less than that calculated for Cl_2O_6 , this being assumed to be due to paramagnetic ClO_3 . It may be noted that the general method had already been tested by Havens‡ for the magnetically somewhat similar system $\text{NO}_2\text{—N}_2\text{O}_4$, for which the equilibrium is well known. Farquarson, Goodeve, and Richardson give the following values for the ClO_3 content and for the equilibrium constant at temperatures between -40° and $+10^\circ$.

TABLE 58

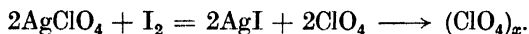
Temperature, ° C.	Percentage of ClO_3 , by weight	$K_c \times 10^3$
−40	0.721	2.54
−30	0.775	2.94
−20	0.826	3.34
−10	0.886	3.85
0	0.943	4.36
+10	1.001	4.91

† J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, 1932, p. 274.

‡ G. G. Havens, *Phys. Rev.* 1932, 41, 337.

Chlorine Tetroxide, ClO₄

It may be noted that the preparation, in dilute solution, of a further oxide of chlorine, ClO₄, which, at any rate in its monomeric form has the additive properties of a free radical, has been claimed by Gomberg† by adding iodine to silver perchlorate in dry ether with precautions against access of moisture and light, the reaction involved being:



It was not found advisable, in preparing the oxide, to exceed concentrations much above 0.1N; and it was not possible to isolate it in a pure state from these dilute ether solutions. Its constitution had therefore to be determined by its reactions.

It reacted quantitatively with many metals (Zn, Cu, Mg, etc.), forming metallic perchlorates; and it readily underwent hydrolysis in the presence of water. Gomberg states that its molecular weight, on the basis of ebulliscopic determinations in ether solution, probably corresponds with (ClO₄)₂.

The formation of ClO₄ was also tested by the production of addition compounds with tri-aryl methyls:‡



In addition to the postulated original reaction leading to the formation of ClO₄ from silver perchlorate and a halogen, some HClO₄ is always produced: indeed, Birkenbach and Goubeau§ are of the opinion that this is the main product of the reaction; and Goodeve|| puts forward the view that the existence of ClO₄ has not been definitely proved.

OXIDES OF BROMINE

Three oxides of bromine, Br₂O, Br₃O₈, and BrO₂, have been prepared, all recently. In addition, a fourth oxide, the composition of which has not yet been established, has been claimed.¶

Bromine Monoxide, Br₂O

The statement contained in earlier literature, that bromine monoxide cannot be formed by a method similar to that used for chlorine

† M. Gomberg, *J. Amer. Chem. Soc.* 1923, **45**, 398.

‡ M. Gomberg and H. R. Gamrath, *Trans. Faraday Soc.* 1934, **30**, 24.

§ L. Birkenbach and J. Goubeau, *Ber.* 1932, **65**, 395.

|| C. F. Goodeve, *Trans. Faraday Soc.* 1934, **30**, 30.

¶ R. Schwarz and H. Wiele, *Naturwiss.* 1938, **26**, 742; *J. prakt. Chem.* 1939, **152**, 157.

monoxide (i.e. by the action of the halogen on mercuric oxide), has now been shown to require revision, in that the activity of mercuric oxide towards bromine has been observed to vary with its mode of preparation. Thus, Zintl and Reinacker† found that, while an oxide made by precipitating hot mercuric chloride solution with excess of sodium hydroxide, followed by drying at 135° , was inactive towards bromine at room temperature, an active oxide could be made by precipitation at lower temperatures.

The following directions are given for the preparation of an active mercuric oxide: 100 g. of mercuric chloride, in 1.5 litres of water, are precipitated at 50° with 100 g. of sodium hydroxide solution with stirring, the soda being added to the mercury salt. The oxide is washed, and dried at 150° in a drying-oven. The adoption of 50° as an optimum precipitation temperature was confirmed by Brenschede and Schumacher,‡ who dried the mercuric oxide at 100 – 110° . On passing bromine vapour over this mercuric oxide, the formation of small concentrations of Br_2O (up to 4–5 per cent. in Zintl and Reinacker's work) was observed, the percentage being determined by iodometric titration coupled with a determination of the total halogen.

The best yields were obtained in a U-tube about 25 cm. high, containing mercuric oxide mixed with glass beads, the distribution of these being arranged so that the bulk of the mercuric oxide was near the outlet of the tube. The optimum temperature was 50 – 60° .

As an alternative method, Brenschede and Schumacher recommend the preparation of Br_2O in carbon tetrachloride solution. This gives concentrations up to 40–50 per cent., counted on the bromine present. In a typical preparation, 10 g. of mercuric oxide and 1.7 c.c. of bromine (5.34 g.) in 100 c.c. of carbon tetrachloride were stirred rapidly for 5 hours at 40° . The oxidation value of the liquid phase (determined iodometrically) was then 32 per cent. higher than that corresponding with its bromine content; and, on adding a further 6 g. of fresh mercuric oxide, and stirring for another 8 hours at 0° , the Br_2O content rose to 40 per cent. In later work a lower second temperature and a somewhat greater proportion of mercuric oxide were employed. Under these conditions, approximately the same

† E. Zintl and G. Reinacker, *Ber.* 1930, **63**, 1098.

‡ W. Brenschede and H. J. Schumacher, *Z. physikal. Chem.* 1935, B **29**, 356; *Z. anorg. Chem.* 1936, **226**, 370.

concentration of Br_2O was obtained, but more quickly: thus 1.7 c.c. of bromine, 90 c.c. of carbon tetrachloride, and 15 g. of mercuric oxide were stirred for 45 minutes at 45° and then for $4\frac{1}{2}$ hours at -18° with the addition of another 20 g. of mercuric oxide. The Br_2O content (based as before on the total bromine present) was about 22 per cent. after the first stage and 42 per cent. after the low-temperature treatment.

Br_2O is also produced by the decomposition of BrO_2 in a high vacuum;† indeed, this method, followed by fractional sublimation to remove any bromine, has been used by Schwarz and Wiele‡ for the preparation of Br_2O in a pure state. The bromine-oxygen ratio in the pure product was established both by decomposing it into bromine and oxygen and by the titrimetric method already mentioned; and the monomeric formula, Br_2O , was confirmed by cryoscopic measurements in carbon tetrachloride solution.

Br_2O is a dark brown solid or liquid, melting at $-17.5 \pm 0.5^\circ$ (Schwarz and Wiele), and is completely stable only below -40° , although it can be preserved for some time at -20° in the dark. It cannot be sublimed without decomposition. The vapour pressure in the liquid state cannot be determined on account of this decomposition but, both as a liquid and as a solid, Br_2O is considerably less volatile than bromine.

Schwarz and Wiele state that a smooth passage of Br_2O to a hypobromite occurs if a solution of Br_2O in carbon tetrachloride is shaken at 0° with an alkali. If, on the other hand, the undiluted oxide is brought into contact with strongly cooled dilute sodium hydroxide solution, bromate is formed as well as hypobromite. Its reaction with water, while in all probability leading primarily to hypobromous acid, is complicated by the decomposition of this acid. Like all bromine oxides, Br_2O liberates iodine from potassium iodide.

Br_3O_8

This oxide has been prepared in a pure state by Lewis and Schumacher§ by the action of ozone on bromine.

The apparatus consisted of a spherical glass reaction vessel, connected with supplies of bromine and of ozone, the latter being made

† R. Schwarz and M. Schmeisser, *Ber.* 1937, **70**, 1163.

‡ Loc. cit.

§ B. Lewis and H. J. Schumacher, *Z. physikal. Chem.* 1928, A **138**, 462; 1929, B **6**, 423; *Z. Elektrochem.* 1929, **35**, 651; *Z. anorg. Chem.* 1929, **182**, 182.

in a state of 95 per cent. purity by Riesenfeld and Schwab's method.† In making the connexions, the use of tap-grease must be avoided. Lewis and Schumacher used glass membrane valves with platinum seats and cones. Bromine is introduced into the evacuated reaction vessel, at a temperature between -5° and $+10^{\circ}$, up to a pressure of 3–15 mm., followed by from 5 to 10 times this amount of substantially pure ozone. The oxide is deposited as a white flocculent solid on the wall of the vessel, the time required for the completion of the reaction varying from about an hour at -5° to 5–10 minutes at $+10^{\circ}$. The temperature and the quantities of bromine and ozone added must be carefully watched, and should be within the above limits, since an excessive temperature or a too high bromine and ozone pressure may lead to a violent explosion. At the temperature of its formation the oxide is stable only in the presence of an excess of ozone. In the absence of this, the deposit usually disappears completely in the course of 2–3 minutes. It can, however, be kept for several days at -80° , even in the absence of ozone.

To determine its composition, Lewis and Schumacher cooled the white deposit to -80° and, after pumping off any ozone and oxygen, allowed the oxide to decompose thermally into its elements. An oxygen-bromine ratio of 2.70 was obtained fairly consistently with a considerable number of specimens, corresponding with a formula $(\text{Br}_3\text{O}_8)_n$.

Br_3O_8 exists in two solid modifications differing in crystal form and stability, the more stable form being obtained as fine white needles by cooling the oxide for several hours to -40° . The transformation is reversible, the transition point being $-35 \pm 3^{\circ}$.

It dissolves in water without the evolution of oxygen or bromine, giving a colourless solution; but titration of the solution with baryta, together with iodometric titration, showed that the acid produced does not correspond with a simple hydration product.

Bromine Dioxide, BrO_2

This oxide has been made‡ by passing a mixture of oxygen and bromine vapour, at a low pressure, through a discharge-tube, part of which is cooled by liquid air. This cooling is necessary since, if the gas mixture is passed first through an ordinary discharge-tube

† E. H. Riesenfeld and G. M. Schwab, *Ber.* 1922, **55**, 2088.

‡ R. Schwarz and M. Schmeisser, *Ber.* 1937, **70**, 1173.

and subsequently through a liquid-air trap, little or no oxide is obtained.

The apparatus used by Schwarz and Schmeisser is shown in Fig. 20. The mixed gas-stream was pumped continuously through the apparatus, at a pressure controlled by the Bodenstein valve, *A*, by means of a rotary oil-pump. The discharge-tube included a lower part, *B*,

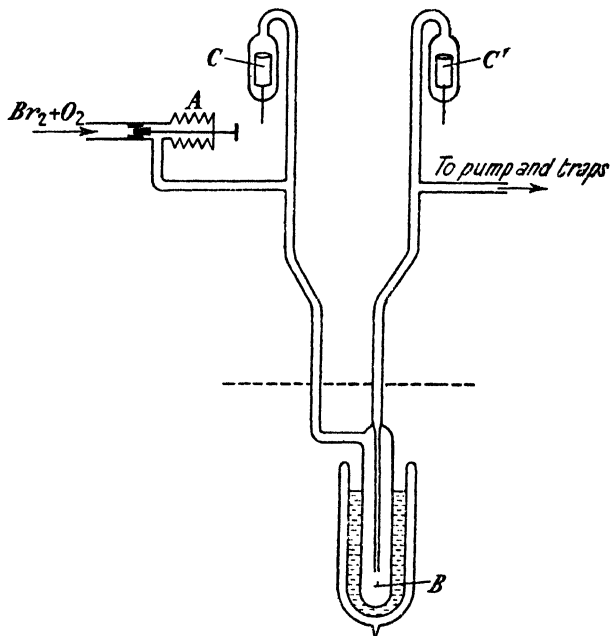


FIG. 20.

of the shape shown, which was immersed in liquid air during the preparation and was subsequently cut off at the level indicated by the dotted line for removal and examination of the product. In later work† ground joints were used in place of cutting the glass. The electrodes, *C* and *C'*, were of sheet aluminium, and the normal current was about 100 milliamperes at 6,000 volts. It was usual, in addition to cooling the lower part in liquid air, also to cool the upper part of the discharge-tube by means of a fan.

The product separated in *B* as a yellowish solid. This part was then cut off and sealed to a receiver cooled with liquid air. After the removal of any bromine from the product by distillation at -30° ,

† R. Schwarz and H. Wiele, *J. prakt. Chem.* 1939, **152**, 157.

the latter was analysed by allowing it to decompose, the bromine-oxygen ratio being found to be approximately 1 to 2 (the observed ratios in two determinations were 1 to 1.97 and 1 to 1.98). The composition was also confirmed by a titration method.

It is stable below -40° , but decomposes at higher temperatures. Schwarz and his collaborators found that, while the thermal decomposition of BrO_2 at atmospheric pressure gives bromine and oxygen, decomposition in a high vacuum leads to brown Br_2O and to a white oxide, the composition of which has not yet been established but which can be separated by fractional condensation. This white body is probably a higher oxide than BrO_2 and may possibly be Br_2O_7 .

BrO_2 has no definite melting-point on account of its instability. It dissolves in carbon tetrachloride with slight decomposition, giving a yellow solution; also in cold water, this solution being colourless. With dilute soda or ammonia, a bromate and bromide are formed. It liberates iodine from potassium iodide.

OXIDES OF IODINE

The only true oxide of iodine capable of stable existence appears to be the pentoxide, I_2O_5 , which has long been known and needs no special comment. It is an ordinary acidic anhydride, forming iodic acid, HIO_3 , with water. The remaining oxygen compounds of iodine, I_2O_4 and I_4O_9 , are in all probability not true oxides but rather iodine iodates. The oxides I_2O_3 and I_2O are unknown in the free state. Their existence in the form of derivatives will be discussed in the following paragraphs and in connexion with the iodine sulphates.

The key to the chemistry of I_2O_4 and I_4O_9 lies, as has recently been emphasized by Masson and Argument,[†] in an appreciation of the basic nature of tervalent iodine. Thus, iodine in this valency state exists mainly in forms in which it is stabilized by association with an acidic partner, both normal iodous salts such as the perchlorate,[‡] $\text{I}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$, or the tri-acetate,[§] $(\text{CH}_3 \cdot \text{COO})_3\text{I}$, being known, as well as basic or iodyl compounds containing the monovalent basic radical, IO^+ , e.g. $(\text{IO})_2\text{SO}_4$. These considerations, and the methods of preparation and properties of the compound, suggest that I_2O_4 is in reality iodyl iodate, $\text{IO} \cdot \text{IO}_3$, rather than a true oxide, IO_2 , of

[†] I. Masson and C. Argument, *J. Chem. Soc.* 1938, 1702.

[‡] P. Schützenberger, *Compt. rend.* 1861, **52**, 135; 1862, **54**, 1026.

[§] F. Fichter, H. Kappeler, and E. Krummenacher, *Z. anorg. Chem.* 1915, **91**, 134.

tetravalent iodine, corresponding with ClO_2 or BrO_2 . This view is usually accepted, although no measurements of its complexity (to differentiate I_2O_4 from IO_2) or of its molecular structure appear to have been made. Similarly, I_4O_6 , in which unusual valencies would have to be assumed if it is to be formulated as an ordinary oxide, has for many years, at the suggestion of Fichter, been regarded as normal iodous iodate, $\text{I}(\text{IO}_3)_3$.

I_2O_4 (or $\text{IO} \cdot \text{IO}_3$)

The early work of Millon on the formation of this oxide by the action of hot sulphuric acid on iodic acid was confirmed and extended by Muir† and by Kappeler‡. Muir gives the following details for its preparation. About 200 g. of concentrated sulphuric acid are added to 60 g. of powdered iodic acid in a platinum dish, the mixture being heated, with stirring, for about 15 minutes, until vapours of iodine begin to be evolved. After being allowed to cool, the dish is kept for several days in a desiccator over sulphuric acid. The yellow crystalline solid is filtered off through glass wool, drained, and transferred to a porous tile and kept in a desiccator for about a week, during which time it is occasionally rubbed to a fine powder and replaced. It is quickly washed on a glass-wool filter with small quantities of cold water, then with small amounts of alcohol until the washings are colourless, and finally with ether. Muir dried the product at 100° ; but Bahl and Partington§ recommend drying at room temperature on a porous plate over quicklime, since some decomposition occurs at 100° . The analysis of four products obtained by Bahl and Partington all corresponded closely to $(\text{IO}_2)_n$.

I_2O_4 is a yellow crystalline solid (sp. gr. 4.2), which is not hygroscopic and is only very slightly soluble in cold water. It is also insoluble in, and unaffected by, dry ether or glacial acetic acid. It dissolves in hot water with decomposition, forming iodic acid and iodine; and it is also acted on slowly by absolute alcohol giving principally I_2O_5 (Muir).

With alkalis, an iodate and iodide are formed:



and, with hydrochloric acid, chlorine is evolved:

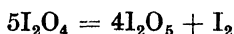


† M. M. P. Muir, *J. Chem. Soc.* 1909, **95**, 656.

‡ H. Kappeler, *Ber.* 1911, **44**, 3496.

§ R. K. Bahl and J. R. Partington, *J. Chem. Soc.* 1935, 1258.

The thermal decomposition of dry I_2O_4 is appreciable at about 85° and is fairly rapid at 135° . Bahl and Partington state that this decomposition leads to the pentoxide, according to the course:



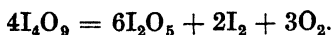
and not to iodine and oxygen, as stated by Muir, although further decomposition to oxygen and iodine is of course obtained at higher temperatures.

I_4O_9 (or $\text{I}(\text{IO}_3)_3$)

This oxide is formed by the action of ozone on iodine. The reaction, which has long been known, has been reinvestigated more recently by Fichter and Rohner† and by Bahl and Partington,‡ the general conditions employed involving either the passage of ozonized oxygen through iodine dissolved in chloroform, carbon tetrachloride, or nitrobenzene or the treatment of dry iodine with ozonized oxygen at $40\text{--}50^\circ$. Bahl and Partington state that, even if the iodine is in solution, the reaction takes place in the vapour phase, and recommend the preparation of the oxide by the action of ozone on iodine vapour. The apparatus used by these authors consisted of a U-tube with bulbs charged with iodine. This was warmed and a current of oxygen containing 8–10 per cent. of ozone was passed through. The yellow product was collected as a solid on a glass-wool filter. Analysis showed it to be substantially pure I_4O_9 .

As an alternative method of preparation, I_4O_9 may be made by heating iodic acid with concentrated (sp. gr. 1.70) phosphoric acid.§ Oxygen, followed at a later stage by iodine, is evolved and a yellowish-white precipitate separates, which is washed with sulphuric acid and dried on a porous plate. This method of making I_4O_9 is somewhat similar to that used for I_2O_4 and, taken in conjunction with the considerations discussed below in the section dealing with iodous sulphates, provides evidence that the two oxides, I_2O_4 and I_4O_9 , are closely related and are both iodates of tervalent iodine.

I_4O_9 is a light yellow powder which, unlike I_2O_4 , is very hygroscopic. It begins to decompose at about 75° , the decomposition taking place according to the equation:

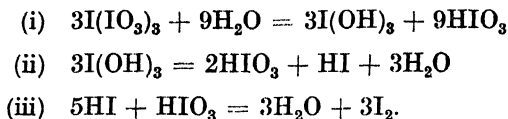


† F. Fichter and F. Rohner, *Ber.* 1909, **42**, 4093.

‡ Loc. cit.

§ F. Fichter, H. Kappeler, and L. Helfer, *Z. anorg. Chem.* 1915, **91**, 134.

With liquid water, free iodine is also produced, the reaction being formulated by Bahl and Partington as proceeding in the following stages:



Treatment of the oxide with hydrochloric acid leads to the oxidation of this to chlorine and to the formation of a yellow solution containing iodine chloride.

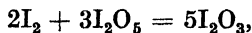
I₂O₃ and the Iodous Sulphates

The chemistry of the iodous sulphates, which occur as intermediate products during the preparation of I₂O₄ by heating iodic acid with sulphuric acid, has been clarified substantially by the recent work of Masson and Argument.†

The yellow iodine sulphate, first prepared by Chrétien‡ and to which various formulae and various degrees of hydration have been ascribed, has now been shown to be I₂O₃.SO₃, i.e. unhydrated iodyl sulphate, (IO)₂SO₄. Masson and Argument regard the heating of iodic acid with sulphuric acid as an acidic stabilization of the basic I₂O₃ (which is unknown in the free state) produced by the thermal decomposition of the pentoxide:



The use of fuming sulphuric acid in place of the ordinary acid is necessary to prevent effectively the further decomposition of the iodine sesquioxide: indeed, on heating I₂O₅ with fuming sulphuric acid (20 per cent. SO₃) to 215–220° in connexion with a gas burette, a brisk evolution of oxygen occurs, which ceases when one mole of O₂ per mole of I₂O₅ has been evolved, no free iodine being produced. Acid-stabilized I₂O₃ was also prepared by the direct action of elementary iodine on I₂O₅ in cold concentrated (92–98 per cent.) sulphuric acid, according to the equation:



the yield being quantitative. The acid-stabilized product obtained by each of the above methods was, in the absence of excessive SO₃,

† Loc. cit.

‡ P. Chrétien, *Compt. rend.* 1896, **123**, 814; *Ann. Chim. Phys.* 1898, **15**, 358.

a finely crystalline, brilliant yellow solid, the analysis of which corresponded with $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ or $(\text{IO})_2\text{SO}_4$. The original method used by Chrétien and later workers, which involved heating iodic acid with sulphuric acid until iodine is evolved, can thus be regarded as a combination of the above two preparative methods (acid stabilization of thermally produced I_2O_3 and direct action of iodine on I_2O_5).

In sulphuric acid containing an excess of SO_3 , Chrétien's yellow sulphate turns into another practically white crystalline sulphate, the composition of which is probably $\text{I}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$. This is thus a compound containing the normal I^{3+} sulphate previously prepared by Fichter, Kappeler, and Helfer.[†] For details of the interesting reverse transformation of the white sulphate to the yellow sulphate, in the course of which I_2O_5 and free iodine are produced temporarily owing to valency bifurcation and subsequent reassembly, reference should be made to Masson and Argument's paper.

In addition to iodic (I^{3+} or IO^+) cations, Masson[‡] has also put forward evidence for the presence of hypoiodous cations, I^+ , in the solutions formed by dissolving iodine in concentrated sulphuric acid containing $\text{I}_2\text{O}_3 \cdot \text{SO}_3$. This cation, I^+ , which is derived from the hypothetical monoxide, I_2O , should, of course, be clearly differentiated from the ordinary iodide anion, I^- .

COVALENT HALOGEN NITRATES

The halogen nitrates constitute a class of interesting covalent substances which has been investigated recently. The fluorine compound has been prepared in the free state; the analogous compounds of the other halogens are known only in the form of derivatives.

Fluorine Nitrate, $\text{F} \cdot \text{NO}_3$

This explosive compound was discovered by Cady,[§] who prepared it by bubbling fluorine through dilute nitric acid.

The apparatus used is shown in Fig. 21. It consisted of a nickel tube, *A*, 1.5 cm. in diameter and 25 cm. long, with the smaller tubes of monel metal. The tip of the fluorine inlet tube, *B*, was of platinum, and the cap, *C*, was fastened lightly by means of cement, since it

[†] F. Fichter, H. Kappeler, and L. Helfer, *Z. anorg. Chem.* 1915, **91**, 134.

[‡] I. Masson, *J. Chem. Soc.* 1938, 1708.

[§] G. H. Cady, *J. Amer. Chem. Soc.* 1934, **56**, 2635.

acted as an explosion door. During the preparation the apparatus was cooled to 0° and cold 3N nitric acid was allowed to flow through continuously at a rate of about 1 litre an hour, the rate of passage of the fluorine, which was considerably diluted with dry air, being about 3 litres an hour. The gas stream from the chamber was led through a glass trap, cooled to -180° , in which a white solid collected. On isolating this trap and allowing it to rise in temperature, a small

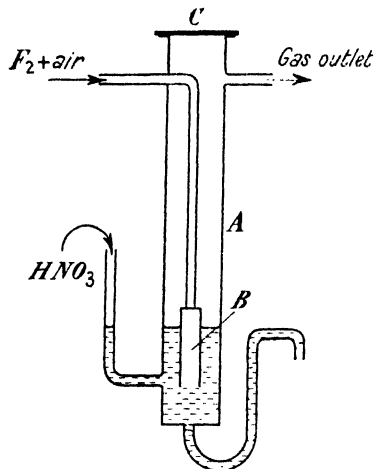
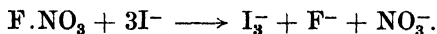


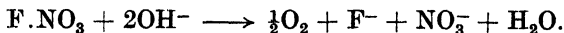
FIG. 21.

quantity of oxygen fluoride was first evolved, and the remainder melted to a colourless liquid which boiled at -42° , the whole passing over within a narrow range. Analysis showed it to possess an empirical formula $(F.NO_3)_n$. Its experimentally determined vapour density was 82 (calculated value 81 for $F.NO_3$), and it is accordingly monomeric. The same compound has also been made by Yost and Beerbower† by the action of solid KNO_3 on fluorine, but no experimental details are given.

Fluorine nitrate has a pungent characteristic odour, somewhat resembling oxygen fluoride, and acts as a strong bronchial irritant. It explodes on heating and sometimes during its preparation; but it can usually be handled safely at room temperature. The gas is moderately soluble in water, with which it reacts slowly, liberating oxygen. It is absorbed completely by potassium iodide solution with liberation of iodine and formation of potassium fluoride, iodide, and nitrate, according to the equation



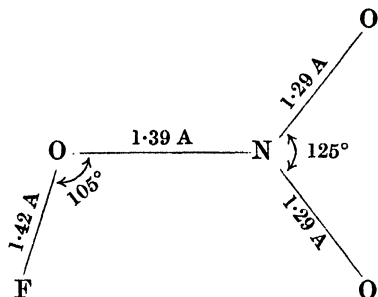
With a solution of potassium hydroxide, it forms potassium nitrate and fluoride and liberates oxygen, the reaction being



The molecular structure of fluorine nitrate, including the interatomic distances and bond angles, has been investigated by electron

† D. M. Yost and A. Beerbower, *J. Amer. Chem. Soc.* 1935, 57, 782.

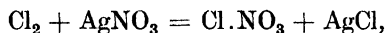
diffraction by Pauling and Brockway,† who assign to it the following configuration:



Other Halogen Nitrates

What appear to be similar compounds of the other halogens have been prepared in association with pyridine by the action of the halogen on silver nitrate in pyridine solution.‡ The complexes have the constitution: $\text{ClNO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, $\text{BrNO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ (also $\text{BrNO}_3 \cdot \text{C}_5\text{H}_5\text{N}$), and $\text{INO}_3 \cdot \text{C}_5\text{H}_5\text{N}$.

The following directions are given for the preparation of the chlorine compound. Nine grams of silver nitrate, previously dried at 120° , are dissolved in 8.75 g. of pyridine and mixed with 50 c.c. of dry chloroform. The solution is added drop by drop to a solution of 4 g. of chlorine in 75 c.c. of chloroform cooled to -35° . This operation is best carried out with mechanical stirring and should take about half an hour. The silver chloride formed by the reaction



is filtered off through glass wool, the whole system being kept at -35° , and to the filtrate are added a further 0.3 g. of pyridine and 175 c.c. of petroleum ether. The addition of the petroleum ether is followed by the formation of a white crystalline precipitate, which is filtered off rapidly, washed three times with 100 c.c. of petroleum ether, and dried for half an hour in a vacuum over sulphuric acid. The yield was 6.2 g. For a successful preparation it is necessary that all materials should be completely water-free. The compound melts, with decomposition, at $77-78^\circ$.

† L. Pauling and L. O. Brockway, *ibid.* 1937, 59, 13; see also Pauling, *Nature of the Chemical Bond*, p. 194.

‡ M. J. Ouchakow and W. O. Tschistow, *J. Gen. Chem. Russ.* 1931, 1, 63, 1258; 1934, 4, 194; 1935, 5, 1387, 1391; *Ber.* 1935, 68, 824; *Bull. Soc. Chim.* (5), 1936, 3, 2142.

INTER-HALOGEN COMPOUNDS

The inter-halogen compounds† which have been prepared up to the present time are summarized below. These are of the general types AB, AB₃, AB₅, and AB₇, in which A and B are both halogens. No inter-halogen compounds containing more than two halogens are known.

TABLE 59

<i>Halides of</i>	<i>Type AB</i>	<i>Type AB₃</i>	<i>Type AB₅</i>	<i>Type AB₇</i>
Chlorine . . .	ClF	ClF ₃	—	—
Bromine . . .	BrF, BrCl	BrF ₃	BrF ₅	—
Iodine . . .	ICl, IBr	ICl ₃	IF ₅	IF ₇

From the above table it will be seen that the power of forming higher polyhalides increases with the atomic number of the halogen, in the sense that the highest covalency shown in the series is 3 for chlorine, 5 for bromine, and 7 for iodine: further, the higher halides are all fluorides.

Some of the compounds, e.g. ICl and ICl₃, have long been known and accordingly need no special description. The preparation of the remaining compounds is largely due to the work of Ruff and his collaborators during the period 1928–34.

CHLORINE FLUORIDES, ClF and ClF₃*Chlorine Monofluoride, ClF*

This was made from the elements‡ by passing separate streams of chlorine and fluorine into a silica T-piece, which was heated externally, as required, by a bunsen flame. The reaction is strongly exothermic and is accompanied by a flame. In a second apparatus the reaction chamber consisted of a cavity in a copper block, which was heated in an oil-bath to 250°. Ruff and Ascher state that, to avoid explosions, fluorine alone should be passed through the block until the reaction temperature has been reached, after which the chlorine may also be led in; but, according to Fredenhagen and Krefft,§ explosions with mixtures of chlorine and fluorine occur only if moisture is present.

The exit gases from the silica T-piece or copper block were passed

† See N. V. Sidgwick, *Ann. Reports Chem. Soc.* 1933, **30**, 128.

‡ O. Ruff and E. Ascher, *Z. anorg. Chem.* 1928, **176**, 258.

§ K. Fredenhagen and O. T. Krefft, *Z. physikal. Chem.* 1929, **141**, 221.

through a series of four copper traps, cooled progressively down to temperatures from -95° to -105° to remove chlorine (m.p. -102° , b.p. -34°) and any ClF_3 (b.p. $+11.3^{\circ}$), and from these to a silica trap at -150° , in which the chlorine fluoride collected as a white solid not greatly contaminated with fluorine (b.p. -188°). It was purified by fractional distillation; and its composition, ClF , was determined both by vapour-density measurements and by chemical analysis.

ClF is, at room temperature, an almost colourless gas with a strong characteristic smell, condensing to a yellowish liquid and to a white solid. According to Ruff and Laas,[†] its melting-point is $-154 \pm 0.5^{\circ}$ and its boiling-point -100.8° . Its vapour pressure in the range -150 to -105° follows the relationship

$$\log p_{(\text{mm.})} = 15.738 - 3109/T + 1.538 \times 10^5/T^2.$$

Calculated values gave the critical temperature as about -14° and the latent heat of vaporization as 2.27 kg.-cals. per mole. The heat of formation, on the basis of a re-calculation by Ruff and Menzel,[‡] is 27.4 kg.-cals.

Chlorine monofluoride is a highly reactive gas differing in many respects both from chlorine and fluorine. For a tabulation of its chemical properties reference should be made to Ruff and Menzel's paper.

Chlorine Trifluoride, ClF_3

ClF_3 has been prepared,[§] in apparatus similar to that used by Ruff and Ascher for ClF , by heating chlorine or ClF with an excess of fluorine. The yield is small; but, on account of its low volatility, separation from the monofluoride is easy. Under favourable conditions Ruff and Krug were able to obtain an exit gas containing about one part of ClF_3 to four parts of ClF .

ClF_3 melts at -83° , forming a light green liquid which boils at $+11.3^{\circ}$. Its vapour pressure is 10 mm. at -71.9° and 495 mm. at 0° . In the gaseous state it is colourless. The calculated critical temperature is 153.5° . It readily attacks glass and is affected even by traces of moisture. Its composition was determined both chemically and by the vapour density.

[†] O. Ruff and F. Laas, *Z. anorg. Chem.* 1929, **183**, 221.

[‡] O. Ruff and W. Menzel, *ibid.* 1931, **198**, 375.

[§] O. Ruff and H. Krug, *ibid.* 1930, **189**, 270.

BROMINE FLUORIDES, BrF , BrF_3 , and BrF_5

All these fluorides are formed by the direct interaction of bromine and fluorine, a mixed product being usually obtained. This, on passage through a condenser tube cooled, for instance, to -150° , yields a series of more or less distinct deposits of the various fluorides in reversed order of volatility.

Bromine Monofluoride, BrF

This compound has not been prepared in a pure state owing to its instability and especially to the ease with which it passes, during fractionation, into other fluorides and free bromine: accordingly, its physical properties are only known approximately. It does not exist in appreciable concentrations above 50° .

For its preparation Ruff and Braidat† recommend passing fluorine and bromine (diluted with 6–10 times its volume of nitrogen) into a reaction chamber consisting of a silica or copper T-piece maintained at 10° . The open end of this T-piece leads downwards into a further silica vessel, also at 10° , in which the BrF_3 formed at the same time is condensed, while the more volatile products pass to silica traps cooled, respectively, to -20° , -50° , -120° , and -180° . The bromine monofluoride is condensed principally in the trap at -120° . Its composition, on the basis of vapour-density measurements and analysis, taking into consideration its degree of purity, corresponded with the formula BrF .

BrF melts at about -33° and boils at $+20^\circ$. In the solid state it consists of crystalline plates somewhat resembling boric acid in appearance, but of the colour of potassium bichromate. The liquid is dark red, and the gas a light red-brown.

Bromine Trifluoride, BrF_3

The direct union of bromine and fluorine was noticed by Moissan;‡ and earlier work on the isolation of the trifluoride was carried out by Lebeau§ and by Prideaux.||

As already stated, BrF_3 collects in the first receiver (at $+10^\circ$) in the apparatus used by Ruff and Braidat for the preparation of BrF .

† O. Ruff and A. Braidat, *Z. anorg. Chem.* 1933, **214**, 81.

‡ H. Moissan, *Le Fluor et ses Composés*, Paris, 1900, p. 123.

§ P. Lebeau, *Compt. rend.* 1905, **141**, 1015; *Bull. Soc. Chim.* (3), 1906, **35**, 148; *Ann. Chim. Phys.* (8), 1906, **9**, 241.

|| E. B. R. Prideaux, *Proc. Chem. Soc.* 1906, **22**, 19; *J. Chem. Soc.* 1906, **89**, 316.

Details for the preparation of pure BrF_3 by this method are contained in an earlier paper by the same authors.[†] The crude product is fractionated in a vacuum, with the distillation vessel at 20° and the receiver at a considerably lower temperature. The use of these low temperatures is necessary, since it attacks silica at higher temperatures: further, in order to minimize contact between any condensed liquid and the connexions, a still of special design was employed, for details of which reference should be made to the paper by Ruff and Menzel[‡] on the preparation of BrF_5 , since the same still was used for purifying the product in each case.

At room temperature, pure BrF_3 is a greenish-yellow liquid which fumes in air and solidifies to greenish-yellow needles. Its melting-point is $+8.8^\circ$ and its boiling-point[§] 127.6° . The density of the liquid at the melting-point is 2.843 and that of the solid is 3.23. In Ruff and Braida's second paper the variation of the vapour pressure of the liquid with the temperature is stated to follow the relationship

$$\log p_{(\text{mm.})} = 8.4195 - 2220.2/T.$$

From the vapour-pressure curve, the latent heat of vaporization should be about 10 kg.-cals. per mole and the critical temperature about 327° . Trouton's constant, $\lambda/T_{\text{b.pt.}}$ is 25.3; and, since this value is higher than that either of bromine (23.2) or of BrF_5 , bromine trifluoride is more associated in the liquid state than these.

Bromine Pentafluoride, BrF_5

This compound has been prepared|| by heating a current of fluorine and pre-formed BrF_3 to about 200° in the platinum apparatus used by Ruff and Keim for the somewhat similar preparation (see later) of IF_7 from IF_5 and fluorine; but with this apparatus an explosion occurred owing to perforation of the platinum and subsequent leakage. It was more simply and safely made, directly from its elements, by leading a current of bromine, diluted with nitrogen, and of fluorine (in excess) through a copper tube heated to 200° by a resistance winding. The exit gases from either type of apparatus were first freed from the less volatile trifluoride (b.p. BrF_3 127.6° ; b.p. BrF_5 40.5°) by an air-cooled condenser, then passed through a trap at -60° , in

[†] O. Ruff and A. Braida, *Z. anorg. Chem.* 1932, **206**, 62.

[‡] O. Ruff and W. Menzel, *ibid.* 1931, **202**, 49.

[§] O. Ruff and A. Braida, *ibid.* 1933, **214**, 91.

|| O. Ruff and W. Menzel, *loc. cit.*

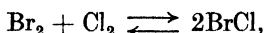
which BrF_5 condensed as a colourless or light yellow liquid, together with a little solid BrF_3 , and finally through a trap at liquid air temperature to condense the excess of fluorine. It was purified by distillation at a low pressure in a silica fractionating apparatus, the column of which was kept at 0° with ice to minimize attack; and it was obtained pure. Its composition was determined, as usual, by its vapour density and analysis.

BrF_5 melts at -61.3° and, as already stated, boils at $40.5 \pm 0.5^\circ$. For its vapour-pressure curve, reference should be made to Ruff and Menzel's paper. Its calculated heat of vaporization is given as 7.433 kg.-cals. per mole. The density of the liquid varies with temperature according to the relationship $d = 3.946 - 0.00346T$. It may be noted that BrF_5 is not appreciably dissociated even at 460° .

BROMINE MONOCHLORIDE, BrCl

This is the only chloride of bromine which has up to the present been recognized. It has not been prepared pure and the evidence for its existence is mainly spectroscopic.

The compound is formed directly† by the reversible reaction



on mixing bromine and chlorine either in the gaseous state or in a suitable solvent (carbon tetrachloride). Its presence may be detected by the colour change or spectro-photometrically by the appearance of a new ultraviolet absorption band, with its maximum at 3,700 Å. The existence of BrCl in mixtures of chlorine and bromine was confirmed by Gray and Style,‡ who also observed its rapid decomposition by the action of light. Barratt and Stein estimate that, starting with an equimolecular mixture of the elements, the compound is formed at room temperature to the extent of about 50 per cent.

The equilibrium
$$K = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]}$$

was further studied by Jost,§ who gives the relationship

$$\log K = \frac{312}{4.57T} + 0.6$$

for the variation of K with the temperature. From this, the heat of formation can be calculated, the value given by Jost being

† S. Barratt and C. P. Stein, *Proc. Roy. Soc.* 1929, A 122, 582.

‡ L. T. M. Gray and D. W. G. Style, *ibid.* 1930, 126, 602.

§ W. Jost, *Z. physikal. Chem.* 1931, A 153, 143.

+0.75±0.5 kg.-cals. per mole. It is accordingly very weakly exothermic. In a later paper, Jost† calculated a value of about 14 kg.-cals. for the activation energy, on the basis of measurements of the reaction velocity.

IODINE FLUORIDES, IF₅ and IF₇

Iodine Pentafluoride, IF₅

This is not a compound which has only recently been made. It was prepared indirectly by Gore,‡ by acting on silver fluoride with iodine, according to the equation



and directly by Moissan (who states that iodine burns with a pale flame in fluorine), also by Prideaux,§ who analysed the product obtained and established its formula as IF₅. It is a colourless liquid boiling at 97° and solidifying at -8°.

Iodine Heptafluoride, IF₇

IF₇ was prepared by Ruff and Keim|| by the further fluorination of IF₅. The apparatus used is shown diagrammatically in Fig. 22. It was made entirely in platinum and consisted of a small bubbling vessel, A, containing liquid IF₅ and maintained at 90°, through which a stream of fluorine was bubbled. The resulting gas mixture passed to a vertical tubular reaction chamber, B, heated to 270° by means of a resistance winding, and subsequently through a reflux condenser, C, by the action of which unreacted IF₅ was returned as a liquid to the bubbler, while the more volatile IF₇ was passed on as a gas and was then condensed by further cooling. The yield was found to increase continuously with the temperature of the reaction tube up to 270°; but temperatures above this could not be used on account

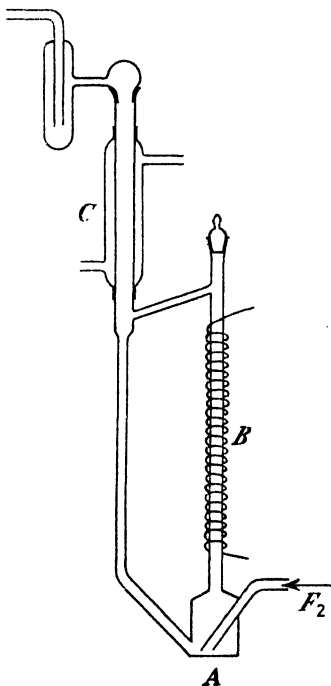


FIG. 22.

† W. Jost, *Z. physikal. Chem.* 1931, B 14, 413.

‡ G. Gore, *Phil. Mag.* (4), 1871, 41, 309; *Chem. News*, 1871, 24, 291.

§ E. B. R. Prideaux, *J. Chem. Soc.* 1906, 89, 316.

|| O. Ruff and R. Keim, *Z. anorg. Chem.* 1930, 193, 176.

of attack on the apparatus. The product was purified by evacuation at -90° , to remove any SiF_4 introduced with the fluorine, and subsequently by fractionation at 0° , with the receiver at -100° , in the absence of air. One such distillation was sufficient to remove the accompanying small quantity of IF_5 ; and the vapour density and analysis of the product then corresponded closely with IF_7 .

IF_7 is a colourless gas at the ordinary temperature, condensing to a snow-white crystalline solid. The vapour pressure of the solid reaches 760 mm. at 4.5° ; and it melts to a mobile colourless liquid under slight pressure at $5-6^{\circ}$. This liquid has a density of 2.75 at the melting-point and a latent heat of vaporization of 7.33 kg.-cals. per mole. The relatively high value of the Trouton constant (26.4) points to some association.

The geometrical structure and probable bond type in the IF_7 molecule, which have not yet been determined, are of great interest on account of the unusual covalency and of the lack of information on the most stable configurations for seven presumably single covalent bonds around a central atom. Two of the fluorine atoms are readily given off, with reversion to one of the better understood pentavalent structures; and there may, of course, be a considerable degree of ionic character both in the 7- and the 5-valent bonding of iodine. It may be noted that, in the case of the somewhat similar ion, $(\text{ZrF}_7)^{3-}$, in which zirconium is also heptavalent, Hampson and Pauling† found that the seventh fluorine atom was apparently accommodated by distorting the normal octahedral structure associated with a hexa-covalent complex.

IODINE CHLORIDES, ICl and ICl_3

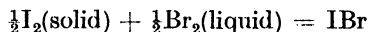
Both of these chlorides have long been known and accordingly will not be dealt with in detail. They are in each case formed by the direct union of the elements. The monochloride exists, in the solid state, in two distinct modifications, melting respectively at 27.2° and 13.9° . The liquid is reddish-brown and boils at 97.4° . Iodine trichloride consists of long lemon-yellow crystals, which readily sublime even at temperatures below 0° . It is easily decomposed into ICl and free chlorine and for this reason its melting- and boiling-points at atmospheric pressure cannot be determined.

† G. C. Hampson and L. Pauling, *J. Amer. Chem. Soc.* 1938, **60**, 2702.

IODINE MONOBROMIDE, IBr

The formation of a bromide of iodine was reported by Balard† as long ago as in 1826; and, although the crystalline solid obtained from equimolecular mixtures of the elements has been regarded generally as a definite compound corresponding with IBr, iodine and bromine form a continuous series of solid solutions; and evidence for the existence of IBr has been based mainly on indirect evidence such as a study of the freezing-point curves of these mixtures.

The equilibrium between bromine and iodine in the gaseous state and in carbon tetrachloride solution has more recently been investigated by McMorris and Yost‡ and by Yost, Anderson, and Skoog,§ who have also determined a number of the thermodynamical constants. The free energy change involved in the reaction



in the above solvent is about -221 cals. per mole, the compound being thus slightly endothermic.

Regularities in Boiling- and Freezing-Points

The simple binary inter-halogen compounds may be regarded as covalent molecules intermediate between those of the components—e.g. F_2 , FCl , Cl_2 —and might accordingly be expected to possess intermediate properties. That this is actually the case is shown, for the freezing- and boiling-points, in Table 60; and, as has been pointed

TABLE 60

	Melting-point, ° C.	Boiling-point, ° C.
F_2	-219	-188
FCl	-154	-100
Cl_2	-102.3	-33.7
F_2	-219	-188
FBr	-33	$+20$
Br_2	-7.2	$+58.8$
Br_2	-7.2	$+58.8$
BrI	$+36$	$+116$
I_2	$+114$	$+184$
Cl_2	-102.3	-33.7
ClI	$\alpha\text{-form} = +27.2$	$+97.4$
	$\beta\text{-form} = +13.9$	
I_2	$+114$	$+184$

† A. J. Balard, *Ann. Chim. Phys.* (2), 1826, **32**, 337.

‡ J. McMorris and D. M. Yost, *J. Amer. Chem. Soc.* 1931, **53**, 2625.

§ D. M. Yost, T. F. Anderson, and F. Skoog, *ibid.* 1933, **55**, 552.

out by Yost and his co-workers, this intermediate relationship also extends to other physical properties and to thermodynamical constants.

The effect of increasing valency, i.e. in a series AB , AB_3 , AB_5 , AB_7 , is less readily generalized, since, in addition to the above influence of the volatility of the components, the increase in molecular complexity tends to raise the boiling-point.

OTHER HALOGEN COMPOUNDS

It is, in a short review of recent progress, obviously only possible to include a limited number of classes of substances or single compounds chosen in each case on grounds of their interest or importance; and, for this reason, two further compounds only will be dealt with in the present section.

Fluorine Cyanide (Cyanogen Fluoride)

Since the cyanogen radical is often regarded as a pseudo-halogen, the halogen cyanides may be viewed as supplementary to the inter-halogen compounds already discussed. All the other halogen cyanides save that of fluorine have long been known; and the preparation of fluorine cyanide thus completes the series.

Fluorine cyanide was made by Cosslett† by the interaction of silver fluoride and cyanogen iodide, the reaction



being carried out either by heating the reactants together in a sealed tube at 220° or by leading the vapour of ICN over solid silver fluoride at the same temperature and condensing the resulting gas in a liquid air trap. The product, after purification by being fractionated at -70° , was shown by analysis and by a vapour-density determination to have the composition FCN . The yield was not high (20–25 per cent.).

FCN is, at low temperatures, a white solid which, at the ordinary pressure, passes into a colourless gas without the formation of a liquid phase, its sublimation pressure being 760 mm. at -72° . From determinations of this pressure at various temperatures, Cosslett calculated a heat of sublimation of about 7 kg.-cals.

† V. E. Cosslett, *Z. anorg. Chem.* 1931, **201**, 75.

This sublimation point is compared with the boiling-points of the other halogen cyanides in the following tabulation:

	FCN	ClCN	BrCN	ICN
Boiling-point (or sublimation point)	—72°	+12.5°	+61.3°	+143.6°
State, at 20°	Gas	Gas	Solid	Solid

It will be seen that, as would be expected, the volatility decreases continuously through the halogen series.

Nitrogen Trifluoride, NF₃

This substance is of special interest, when compared with the corresponding nitrogen compounds of the other halogens, by reason of its positive heat of formation. It is accordingly non-explosive.

NF₃ was first prepared by Ruff, Fischer, and Luft† by the electrolysis of molten NH₄F.HF in a copper cell at 125°. Owing to the presence of traces of water in the electrolyte, the electrolysis gas contained, in addition to nitrogen fluorides (including the intermediate molecules, NH₂F and NHF₂), also ozone, oxygen, and nitrous oxide, as well as hydrogen, nitrogen, and some HF. The gas was accordingly passed, in copper apparatus, through dry granular KF to remove HF and water, and over MnO₂ for the catalytic conversion of any ozone to oxygen. In the absence of a reagent to remove ozone, explosions were apt to occur. From this point the apparatus was of glass and consisted of three progressively cooled traps. In the first of these, at —75°, the removal of HF was completed. The second and third traps were cooled, respectively, with ordinary liquid air and with liquid air cooled further by having hydrogen bubbled through it. To prevent the condensation of oxygen a stream of nitrogen was passed through the whole apparatus during the electrolysis.

The product which condensed in the last two traps consisted of a colourless liquid (crude NF₃) together with some solid N₂O. This impurity, also any SiF₄ formed by attack on the glass, was eliminated by fractionation at —160°; and any NH₂F or NHF₂ could be removed‡ by allowing the gaseous NF₃ to stand, in the absence of air, in contact with dilute sodium hydroxide solution, which hydrolyses these

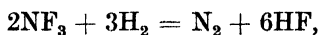
† O. Ruff, J. Fischer, and F. Luft, *Z. anorg. Chem.* 1928, **172**, 423.

‡ O. Ruff, *ibid.* 1931, **197**, 273.

impurities but does not attack NF_3 . The density indicated a mol. wt. of 71 ($\text{NF}_3 = 70$). Its composition was also confirmed by analysis. As a criterion of purity, Ruff states that it should remain clear at -190° and that any turbidity or precipitate probably indicates the presence of N_2O .

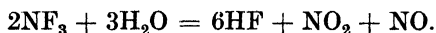
NF_3 is also formed by the direct fluorination of ammonia. Although, with undiluted gases, the reaction is so violent that the ammonia is for the most part destroyed, Ruff and Hanke† have shown that some NF_3 can be isolated if the ammonia used is diluted with nitrogen. The product also contains NH_2F and NHF_2 .

Nitrogen trifluoride melts at -216.6° , boils at -120° , and has a vapour pressure of 3 mm. at -183° , 49 mm. at -160° , and 325 mm. at -135° . Its latent heat of vaporization is 2,400 cal.; and its heat of formation, as determined by Ruff and Wallauer‡ by measurements of the heat effect in the reaction



is $+26 \pm 2$ kg.-cals.

Nitrogen fluoride is a relatively stable gas, which is almost insoluble in water. It is not decomposed by sparking and does not attack glass; and it may be liquefied and stored in steel cylinders, which are cooled with liquid air during the filling. While it is not acted on by water under ordinary conditions, a reaction occurs with a bluish flame on sparking a mixture of NF_3 and water vapour and spreads slowly through the gas with production of brown oxides of nitrogen according to the equation



A mixture of the fluoride with hydrogen explodes on being sparked, the reaction following the equation already given.

† O. Ruff and E. Hanke, *Z. anorg. Chem.* 1931, **197**, 395.

‡ O. Ruff and H. Wallauer, *ibid.* 1931, **196**, 421.

IV
HAFNIUM
(ELEMENT 72)

THE reason for the relatively late discovery of hafnium (by Coster and Hevesy in 1922) lies not in its rarity but in its very close similarity to zirconium.

As has been emphasized by Hevesy,† twin elements, represented by zirconium and Element 72, would be expected in Group IVa, corresponding (see Table 61) with analogous twin pairs in Groups Va and VIa; but the degree of resemblance of hafnium to zirconium far exceeds that of niobium to tantalum, or of molybdenum to tungsten: indeed, the chemistry of hafnium is, for all practical purposes, identical with that of zirconium; and such points of difference as exist lie in secondary properties such as in the relative solubility or relative stability of corresponding compounds.

TABLE 61

<i>Group</i>		
<i>IVa</i>	<i>Va</i>	<i>VIa</i>
Zr (40)	Nb (41)	Mo (42)
Hf (72)	Ta (73)	W (74)

For this reason some hafnium almost always accompanies zirconium in its minerals. The percentage of hafnium is often considerable: thus, the zircons (zirconium silicates) ordinarily contain from 1 to 7 per cent. of hafnium; and certain secondary zirconium minerals, such as alvite and cyrtolith, may contain from 20 to 30 per cent. of hafnium,‡ these percentages being on the total metal (Zr+Hf) present. The hafnium content is sufficient to affect appreciably the apparent atomic weight of zirconium from various sources and probably explains the appreciable variation in the atomic weight of zirconium arrived at by various investigators,§ since each 1 per cent. of hafnia in zirconia would raise the apparent atomic weight of the zirconium by 0.6 atomic unit (Zr = 91.2; Hf = 178.6).

† G. v. Hevesy, *Das Element Hafnium*, J. Springer, Berlin, 1927.

‡ G. v. Hevesy, *Chem. and Ind.* 1923, 42, 929.

§ See G. v. Hevesy, *Chem. Reviews*, 1926, 2, 1.

Discovery of Hafnium

The discovery of hafnium is an outstanding example of the use of Moseley's X-ray spectroscopic law to fix the atomic number of an unknown element. According to this law, the frequency of corresponding lines in the same (K , L , M , etc.) series of the X-ray spectra of the elements is a simple function of the atomic number of the element responsible for the spectral line in question, a linear graph being obtained by plotting $\sqrt{\nu}$ (or $\sqrt{1/\lambda}$) against Z . From a general graph of this nature, the wave-lengths of the lines for an unknown element can be obtained by interpolation. In general, each element gives, in each series, a number of successive lines known as the α , β , γ , and higher lines, each of these lines being capable of further resolution into α_1 and α_2 , β_1 and β_2 , etc.

The X-ray spectroscopic analysis even of the first Norwegian zircon examined by Coster and Hevesy† showed at once the α_1 and α_2 lines in the L -spectrum in exactly the positions which could be calculated for an element of atomic number 72. Shortly afterwards the β_1 and β_2 lines were also identified. This direct observation of the X-ray spectrum, without a process of preliminary enrichment such as was necessary, for instance, for the element rhenium (see Chapter V), indicated that Element 72 was present in considerable quantity. The new element was named hafnium (Hafnia = Copenhagen).

As a result of this observation a systematic X-ray spectroscopic examination was made of a large number of zirconium minerals; and a method—consisting in the addition‡ of a known percentage of tantalum to the finely ground mineral and in comparing the intensity of the Hf and Ta lines—was worked out for assessing their hafnium content without chemical treatment.

SEPARATION OF HAFNIUM FROM ZIRCONIUM

This separation has been carried out by two main methods:

- (i) Fractional crystallization, especially of double fluorides.
- (ii) Fractional precipitation, including methods based on the lesser stability of complexes containing hafnium.

In addition, some separation can be obtained in a number of other ways, including the fractional sublimation of halides or oxyhalides and the fractional decomposition of the sulphates, the peroxides, or

† D. Coster and G. v. Hevesy, *Nature*, 1923, **111**, 79, 182, 252.

‡ G. v. Hevesy, *Ber.* 1923, **56**, 1503.

the complex fluorides; but these methods have proved far less effective.

Separation by Fractional Crystallization

A suitable salt for the first stage of the concentration of hafnium by this method is the ammonium hexafluoride, $(\text{NH}_4)_2\text{MF}_6$, in which M is Hf or Zr. The solubilities, at 20°, of these salts and of the corresponding potassium compounds (which were used at a later stage in the concentration) are given in Table 62. The solubilities are expressed in g.-mols. per litre.

TABLE 62

<i>Salt</i>	<i>Solvent</i>	<i>Solubility of Hf compound</i>	<i>Solubility of Zr compound</i>
$(\text{NH}_4)_2\text{MF}_6$. . .	Water	1.425	1.050
K_2MF_6 . . .	0.125N-HF	0.1008	0.0655
„ . . .	5.89N-HF	0.1942	0.1297

It will be seen that in every case the hafnium salt is more soluble than the corresponding zirconium compound: consequently the hafnium is progressively concentrated in the mother liquors. Further, the ammonium salts are far more soluble than the potassium salts. In addition to the hexafluorides, both hafnium and zirconium form heptafluorides of the type $(\text{NH}_4)_3\text{HfF}_7$. Since, however, the difference in the solubility of these hepta salts of hafnium and zirconium is far less than for the hexafluorides, it is necessary to avoid the formation of the hepta compounds by not adding more than 2 g.-mols. of alkali fluoride for each g.-atom of zirconium or hafnium present.

In a typical concentration by this method, Hevesy† started with about 2 kg. of ammonium zirconium hexafluoride containing about 3 per cent. of hafnium and, using a technique similar to that used for rare earth separations, was able, after a large number of re-crystallizations, to obtain ten fractions, weighing in all 300 g. and containing from 30 to 80 per cent. of hafnium. This was then converted to the less soluble potassium salt and the fractionation was continued. After many further crystallizations the best fractions of the potassium salt were found to be substantially free from zirconium, although they still contained some columbium and iron. These were removed by converting the hafnium compound into the oxide (by

† G. v. Hevesy, *Chem. Reviews*, loc. cit.

treatment with sulphuric acid, ignition of the sulphate and extraction of the potassium sulphate with hot water), followed by the conversion of the hafnia into the neutral sulphate. On keeping a solution of this for some days at 40° , a basic salt, free from impurities, was precipitated. This was converted into hafnium hydroxide, then into oxychloride by solution in hydrochloric acid, the HfOCl_2 being finally recrystallized 8 times from concentrated hydrochloric acid. Hafnium dioxide prepared from the last fractions of the oxychloride contained only between 0.16 and 0.57 per cent. of ZrO_2 .

In place of using the complex hexafluorides for the separation, the oxychlorides may be recrystallized from hydrochloric acid. This method has already been mentioned in the preceding paragraph as a final step in the hexafluoride separation. As will be seen from Table 63, the solubility both of hafnium and of zirconium oxychloride is greatly increased by increasing the strength of the acid used as the solvent, this being probably due to the formation of a complex, H_2HfOCl_4 ; further, at high hydrochloric acid concentrations, zirconium hydrochloride is the more soluble, so that in this case the hafnium is concentrated in the crystals in place of in the mother liquor, as with the hexafluorides. This is of considerable practical importance, since the impurities tend to accumulate in the liquor. The solubilities given in the table are, as before, at 20° and in g.-mols. per litre.

TABLE 63
Solubilities of Oxychlorides in aq. HCl

<i>Normality of HCl</i>	HfOCl_2	ZrOCl_2
6.35	—	0.1037
6.48	0.1030	—
10.94	—	0.205
11.28	0.1509	—
11.61	—	0.334

Fractionation by recrystallization may also be carried out with other salts, e.g. the complex oxalates or ammonium zirconium (hafnium) sulphate; but the results are less satisfactory.

Separation by Fractional Precipitation

Hevesy and his co-workers have examined a large number of fractional precipitation methods. Whether hafnium, on the one

hand, or zirconium, on the other, can by repeated precipitation be progressively concentrated in the first portions of the precipitate depends on a number of factors, including the relative solubility of the zirconium or hafnium compound precipitated, the generally greater ease of decomposition of co-ordination complexes containing hafnium as the central atom,[†] and the slightly greater basicity of hafnia compared with zirconia.

Hevesy found that, on fractionally precipitating a solution of the mixed oxychlorides with ammonia or other bases, the zirconium content of the first fractions of the precipitate was less than that of later fractions: similar results were obtained by fractional precipitation with benzoic acid. Probably the most successful precipitation from the standpoint of separation is, however, as the phosphate. Hevesy[‡] observed that, if sodium phosphate is added to a strong nitric or hydrochloric acid solution of a zirconium salt containing hafnium, the hafnium is concentrated in the first fractions of the precipitate; and phosphate precipitation has been developed both by him and by de Boer.

According to de Boer's modification of the method,[§] a sulphuric acid solution of the mixed zirconium and hafnium complex sulphates, of the type $\text{H}_2\text{Zr}(\text{SO}_4)_3$, containing a regulated amount of phosphoric acid (insufficient for the complete formation of zirconium or hafnium phosphate), is fractionally decomposed by the addition of water. As a result both of the somewhat greater ease of decomposition of the hafnium complex and of the lesser solubility of hafnium phosphate, the progressive concentration of the hafnium in the precipitate is relatively rapid; and it was found possible to obtain substantially pure hafnium phosphate after only twelve to fifteen fractional precipitations.

A further method,^{||} which has been used for the preparation of hafnium from a zircon mineral (malakon), consists in fractionally decomposing the complex phosphate-fluoride compound, obtained by dissolving zirconium or hafnium phosphate in hydrofluoric acid, by means of borax, the phosphate being re-precipitated. The hafnium content of the zirconium in the mineral treated was 3–4 per cent. By following a special precipitation technique, for details of which

[†] J. H. de Boer, *Z. anorg. Chem.* 1927, **165**, 1.

[‡] G. v. Hevesy, *Ber.* 1923, **56**, 1503.

[§] J. H. de Boer, *Z. anorg. Chem.* 1927, **165**, 16.

^{||} J. H. de Boer and P. Koets, *ibid.*, p. 21.

reference should be made to the original paper, about twelve precipitations led to a phosphate in which the hafnium content was 55 per cent. of the total metal (Zr+Hf) present. This was further purified by the sulphuric acid method described in the last paragraph.

Another process† for the separation of hafnium from zirconium is based on fractional precipitation as ferrocyanide, the first fractions being richer in hafnium. For instance, on adding sodium ferrocyanide to zirconia (containing about 1 per cent. of hafnia) in sulphuric-oxalic acid solution, about 60 per cent. of the total hafnium present was concentrated in the first fractional precipitate. This otherwise promising method is, however, not suitable‡ for the extraction of hafnium from its minerals, since the usual presence of phosphorus in these minerals causes the hafnium ferrocyanide to be contaminated with hafnium phosphate.

Metallic Hafnium

Elementary hafnium was first made by Hevesy by reducing potassium hafnium hexafluoride with sodium, the method being similar to a well-known one for the preparation of zirconium.

Its production in a pure state, free from zirconium, has been studied in considerable detail by de Boer and his co-workers.§ The methods used include:

- (i) The reduction of HfCl_4 by sodium at about 850° .
- (ii) The reduction of HfO_2 with magnesium and sodium or with calcium and sodium, in each case at about $1,300^\circ$.
- (iii) The thermal decomposition of HfI_4 on an electrically heated tungsten filament at about $1,800^\circ$. The hafnium filament produced in this way has a tungsten core.

Special precautions and repeated preparation (for details of which the original papers should be consulted) were found to be necessary in order to obtain a pure product. Hafnium, when pure, is very ductile and can readily be hammered, drawn, or rolled. Some of its principal properties, compared with those of zirconium, are given in Table 64.

† W. Prandtl, *Z. anorg. Chem.* 1932, **208**, 420; W. C. Schumb and F. K. Pittmann, *Ind. and Eng. Chem. (Anal. Ed.)*, 1942, **14**, 512.

‡ W. Prandtl, G. Mayer, and L. Buttner, *Z. anorg. Chem.* 1937, **230**, 419.

§ A. E. van Arkel and J. H. de Boer, *ibid.* 1925, **148**, 345; J. H. de Boer and J. D. Fast, *ibid.* 1926, **153**, 1; 1930, **187**, 177, 193.

TABLE 64

	Hf	Zr
Density	13.31	6.52
Melting-point, ° Abs.	c. 2500	2130
Atomic volume, in A ³	13.42	13.97
Electrical resistance at 0° C.; $\rho \times 10^4$ (in Ω cm.).	0.30	0.41
Temp. coeff. of electrical resistance; $\alpha \times 10^2$.	0.44	0.44

The density and atomic volume have also been calculated, from X-ray data, by van Arkel,† who gives the following values:

	Hf	Zr
Density	13.08 ± 0.05	6.53 ± 0.01
Atomic volume	13.66 ± 0.06	13.97 ± 0.02

These values agree for zirconium but are lower for the density of hafnium, and higher for its atomic volume, than those contained in Table 64. It is probable that the figures given in the table are the more accurate. Further work on the resistance of hafnium at low temperatures (1.3° to 90° Abs.) has been carried out by de Haas and Voogd.‡ The atomic heat of hafnium at low temperatures has also been studied.§ This shows a sharp maximum at 75° Abs. and rises from 5.4 at 100° to 6.0 at 200° Abs.

Isotopes and Atomic Weight

The atomic weight has been determined chemically by Hönigschmid and Zintl|| by the gravimetric analysis of hafnium tetrabromide. After a correction for a small known zirconium content, values of 178.57 and 178.64 were obtained in two determinations. The international value is 178.6.

The abundances of the principal isotopes of hafnium, according to Aston,¶ are as follows:

Mass number	176	177	178	179	180
Percentage abundance	5	19	28	18	30

Aston's figures, after a necessary correction, give an atomic weight

† A. E. van Arkel, *Z. physikal. Chem.* 1927, **130**, 100.

‡ W. J. de Haas and J. Voogd, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 707.

§ S. Critescu and F. Simon, *Z. physikal. Chem.* 1934, B **25**, 273.

|| O. Hönigschmid and E. Zintl, *Z. anorg. Chem.* 1924, **140**, 335; *Ber.* 1925, **58**, 453.

¶ F. W. Aston, *Proc. Roy. Soc.* 1935, A **149**, 396; *Nature*, 1934, **133**, 684.

of 178.4 ± 0.2 , in fair agreement with the international value, 178.6. A further isotope, ^{174}Hf , with a probable abundance of about 0.3 per cent., has been detected by Dempster;† and there was also some indication of a little ^{172}Hf .

OXIDES OF HAFNIUM

Hafnium Dioxide, HfO_2

This oxide can be made by all the methods ordinarily used for the preparation of zirconia, for instance, by precipitating a hafnium salt with ammonia or by igniting hafnium sulphate or oxychloride in air. Like zirconia, it probably also exists in the hydrated form as hafnium hydroxide, $\text{Hf}(\text{OH})_4$. Its reactions show it to be slightly more basic than zirconia.

Hafnium dioxide is a white powder which, when prepared by igniting the sulphate first at a moderate temperature and then at $1,000^\circ$, has a density‡ of 9.7 ($\text{ZrO}_2 = 5.73$). The density varies a little with the method of preparation; but, by reason of the considerable difference between the values for hafnia and zirconia, the density of a mixed oxide made in the above manner may be used as a convenient measure of the ratio of hafnium to zirconium in the sulphate which has been ignited. If d is the density, at 20° , the percentage of hafnium, x , in the hafnium-zirconium mixture can be derived from the relationship

$$x = \frac{d - 5.73}{0.0394}.$$

Its melting-point is given by Clausing§ as $3047 \pm 25^\circ$ Abs. ($\text{ZrO}_2 = 2950 \pm 20^\circ$).

Hafnium Peroxide

Like titanium and zirconium, hafnium salts form a hydrated peroxide or per-acid on treatment with hydrogen peroxide either in alkaline or in acid solution.|| Thus it is produced by precipitating a hafnium sulphate solution with hydrogen peroxide and ammonia. The dehydration of the colloidal precipitate is best carried out by extraction with liquid ammonia; and the product then has a com-

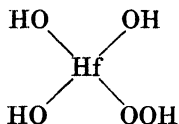
† A. J. Dempster, *Phys. Rev.* 1939, **55**, 794.

‡ G. v. Hevesy and V. Berglund, *J. Chem. Soc.* 1924, **125**, 2372.

§ P. Clausing, *Z. anorg. Chem.* 1932, **204**, 33.

|| R. Schwarz and H. Giese, *ibid.* 1928, **176**, 209.

position $\text{HfO}_3 \cdot 2\text{H}_2\text{O}$. Schwarz and Giese ascribe to this the structural formula



and obtained peroxides (or per-acids) of analogous composition from zirconium and titanium.

Hafnium peroxide is stable at room temperature. It decomposes at a higher temperature, but is somewhat more stable than the corresponding zirconium compound. Hevesy has used this greater stability of hafnium peroxide precipitated in alkaline solution by hydrogen peroxide as a partial separation method from zirconium, the mixed peroxide being allowed to remain at $40\text{--}50^\circ$. Unlike the zirconium compound, hafnium peroxide is stated to be almost completely insoluble in ice-cold hydrogen peroxide. This property has been suggested as a basis for separation.

HAFNIUM HALIDES AND OXYHALIDES

As is the case throughout the whole of the chemistry of hafnium, the same methods of preparation can be used as have long been known for the corresponding zirconium compounds; and, in the following sections, emphasis can be laid only on differences in physical properties and on the actual methods of preparation which have been employed in the course of the relatively small volume of work which has been published on hafnium as distinct from zirconium compounds.

Hafnium Tetrafluoride, HfF_4

This has been prepared† by heating the easily made double salt, $(\text{NH}_4)_2\text{HfF}_6$, in a platinum or nickel boat in a current of nitrogen. Unlike ZrF_4 it is stable in moist air and is only slowly attacked by hot mineral acids or alkalis.

It is readily volatile at high temperatures and may be partially separated from ZrF_4 by sublimation in nitrogen at $800\text{--}850^\circ$ or at 530° in a vacuum. This sublimation can also be used to separate hafnium and zirconium from iron, etc.

The alkali double fluorides, of the types K_2HfF_6 and K_3HfF_7 , are easily accessible compounds, since mixtures of these with the

† G. v. Hevesy and W. Dullenkopf, *ibid.* 1934, **221**, 161.

zirconium double fluorides are produced by the ordinary method of extracting zirconium from its minerals, namely, by fusion with acid potassium fluoride and extraction with boiling water. They are also formed directly, by adding potassium or ammonium fluoride to a solution of hafnium fluoride. These double salts crystallize well. The crystal structure of $(\text{NH}_4)_3\text{HfF}_7$ has been studied, by X-ray methods, by Hassel and Mark,[†] the volume of the elementary cube, containing four molecules, being 830.6 \AA^3 for $(\text{NH}_4)_3\text{HfF}_7$ and 818.2 \AA^3 for the zirconium salt. The molecular volumes per molecule are given as 125.7 and 123.9 \AA^3 , the hafnium compound being about 1.5 per cent. larger than the zirconium salt.

Hafnium Tetrachloride and Tetrabromide, HfCl_4 and HfBr_4

De Boer and Fast[‡] prepared the tetrachloride by the method used by Lely and Hamburger for zirconium tetrachloride. Hafnium dioxide was heated in a current of chlorine saturated with carbon tetrachloride in a porcelain tube at 800° . The product condensed in a further part of the tube, kept at about 200° , as a well-crystallized coherent mass.

HfCl_4 melts at 432° , and HfBr_4 at 420° ;[§] but each of these halides has a sublimation pressure which reaches 760 mm. below the melting-point. The sublimation temperatures are given in Table 65.

TABLE 65

<i>Halide</i>	<i>Temp. at which $p_{\text{subl.}} = 760 \text{ mm.}$ $^\circ \text{C.}$</i>	<i>Calculated heat of sublimation in kg.-cals. per mole</i>
HfCl_4 . .	317	24
HfBr_4 . .	322	24
ZrBr_4 . .	357	—

Hafnium Tetraiodide, HfI_4

This is most easily made by synthesis from its elements|| by a method similar to that used for ZrI_4 . Iodine and a slight excess of the finely divided metal are introduced separately into two connected glass bulbs, which are then evacuated and sealed off. On heating the system, first of all gently and then to $400\text{--}500^\circ$, the iodine vapours

[†] O. Hassel and H. Mark, *Z. Physik*, 1924, **27**, 89; G. v. Hevesy, *Chem. Reviews*, loc. cit., p. 18. [‡] J. H. de Boer and J. D. Fast, *Z. anorg. Chem.* 1930, **187**, 193.

[§] W. Fischer, R. Gewehr, and H. Wingchen, *ibid.* 1939, **242**, 161.

|| J. H. de Boer and J. D. Fast, *ibid.* 1926, **153**, 1.

pass into the bulb containing the hafnium and combination takes place with incandescence.

Hafnium iodide has been used for the preparation of metallic hafnium by decomposition on a tungsten filament. Its general properties do not appear to have been described; but the corresponding zirconium iodide is a reddish-brown crystalline powder, which is very hygroscopic and dissolves in water to form ZrOI_2 . It is also attacked by dry oxygen at 100° and burns at higher temperatures to the oxide and free iodine.

Hafnium Oxyhalides, HfOCl_2 , etc.

The preparation of hafnium oxychloride from hafnium phosphate (in which form hafnium is easily precipitated) has been described by de Boer and Broos.[†] The phosphate is dissolved in hydrofluoric acid and the hafnium precipitated at the hydroxide. This is then redissolved in hydrochloric acid and re-precipitated with ammonia. The precipitate usually contains some silica, which is removed by repeated solution in hydrochloric acid and evaporation to dryness. The final solution in hydrochloric acid is then evaporated to incipient crystallization and cooled, when pure $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ crystallizes out in long needles.

HAFNIUM SULPHATE

Hafnium sulphates are formed by dissolving hafnium hydroxide in sulphuric acid, by the action of fuming sulphuric acid on hafnium chloride, or by dissolving hafnium dioxide in 40 per cent. hydrofluoric acid followed by repeated 'fuming off' with concentrated sulphuric acid;[‡] but, especially if an excess of strong sulphuric acid is used, the product contains complex sulphates, possibly of the type $\text{H}_2\text{Hf}(\text{SO}_4)_3$, in addition to the normal sulphate, $\text{Hf}(\text{SO}_4)_2$. Hevesy and Cremer found that some excess of sulphuric acid is always present in hafnium sulphate, although the amount varies with the method of preparation. The excess is very tightly held and can be removed by heating only to temperatures at which hafnium sulphate itself begins to decompose.

Hafnium sulphate is somewhat more stable towards heat than zirconium sulphate, in conformity with the slightly greater basicity of hafnia. Consequently, the decomposition pressure of hafnium sulphate is less, at a given temperature, than that of zirconium

[†] J. H. de Boer and J. Broos, *ibid.* 1930, 187, 192.

[‡] G. v. Hevesy and E. Cremer, *ibid.* 1931, 195, 339.

sulphate. Some decomposition pressures, from the measurements of Hevesy and Cremer, are given in Table 66. The subject is of interest since the fractional decomposition of the mixed sulphates by heat has been used for the partial separation of hafnium from zirconium. The method is, however, as has already been mentioned, not so effective as fractional crystallization.

TABLE 66

Relative Decomposition Pressures of Hafnium and Zirconium Sulphates

Temperature, ° C.	Decomposition pressure, in mm.	
	Hf	Zr
576	1.2	6.3
598	3.1	15
610	5.6	24
620	—	42
632	27	110

It may be noted that the tendency towards the formation of complexes, which is common both to hafnium and to zirconium, is shown by many types of compounds in addition to the sulphates, and that this complex formation readily occurs both in alkaline and in acid solution. Thus, complex carbonates result on adding alkali carbonates to a solution of hafnium or zirconium oxychloride; and hafnium phosphate dissolves in strong sulphuric acid, in hydrofluoric acid, or in oxalic acid, with formation of what are probably coordination complexes. In general, the zirconium complex is more stable than the corresponding hafnium compound, i.e. zirconium goes more easily into solution in the presence of a complex-forming substance or, conversely, a hafnium complex is more easily broken up on dilution. For instance, on diluting the complex solution of mixed hafnium and zirconium phosphates in sulphuric acid, the hafnium phosphate tends to be re-precipitated first. This greater tendency of zirconium to form coordination compounds has been ascribed by de Boer to differences in the ionic radius of hafnium and zirconium.†

HAFNIUM PHOSPHATE AND ARSENATE

Like zirconium, hafnium differs from the other metals (except niobium, which can be separated by other methods) in forming a phosphate which is only very slightly soluble in strong hydrochloric

† J. H. de Boer, *Z. anorg. Chem.* 1927, **165**, 1.

or nitric acid: consequently hafnium phosphate is a readily accessible compound, since it is precipitated on adding, for instance, sodium phosphate to a strongly acid solution of a hafnium salt.

Hevesy and Kimura† dissolved 2 g. of hafnium oxychloride in 6N-hydrochloric acid and precipitated this by adding 2 g. of disodium phosphate in 1.5 litres of hydrochloric acid of the same strength. The compound which was precipitated had a composition, $\text{HfO}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. On ignition it lost $2\text{H}_2\text{O}$.

Hafnium phosphate is less soluble in hydrochloric acid than zirconium phosphate, and the solubilities increase with an increase in the normality of the acid. The solubilities, at 20° , expressed in moles of $\text{MO}(\text{H}_2\text{PO}_4)_2$ per litre of solution, are contained in Table 67.

TABLE 67

Solubilities of Hf and Zr Phosphates in Hydrochloric Acid

Normality of HCl	Solubilities	
	Hf	Zr
5.94	0.00009	—
6.01	—	0.00012
10.00	—	0.00023
10.21	0.00012	—
10.48	0.00013	—

The arsenates of hafnium and zirconium‡ are also very insoluble in hydrochloric acid. Their general solubility appears, however, to be greater than that of the phosphates, since they are fairly soluble in 50 per cent. sulphuric acid, which is not the case with the phosphates; and, on diluting the solution, the arsenates are not precipitated. Like the phosphates, they dissolve in strong sulphuric acid, and in hydrofluoric or oxalic acid, with formation of complexes.

The arsenates can be dissolved in concentrated nitric acid and can be re-precipitated by dilution with water, the hafnium arsenate being less soluble than zirconium arsenate. This method can be used for fractionation, the hafnium accumulating preferentially in the precipitate. De Boer states that an especially good fractionation is obtained if the arsenic acid is formed in the solution itself, by oxidizing arsenious oxide in hydrochloric acid in the presence of mixed zirconium and hafnium oxychlorides.

† G. v. Hevesy and K. Kimura, *J. Amer. Chem. Soc.* 1925, **47**, 2540.

‡ J. H. de Boer, *Z. anorg. Chem.* 1927, **165**, 14.

V

MASURIUM AND RHENIUM

(ELEMENTS 43 AND 75)

NEW ELEMENTS OF THE MANGANESE GROUP

UNTIL about 1925, the seventh vertical column of the periodic system contained three gaps, two of which (Elements 43 and 75) were in the manganese group and the third (Element 85) presumably in the halogens. The position of these vacant spaces is given in Table 68, which also shows the nearest horizontal neighbours of the missing homologues of manganese.

TABLE 68

<i>VIa</i>	<i>Group</i>		<i>VIII</i>
	<i>VIIa</i>	<i>VIIb</i>	
		F	
		Cl	
Cr 24	Mn 25		Fe 26
		Br	
Mo 42	Ma 43		Ru 44
		I	
W 74	Re 75		Os 76
		— 85	

Reference to the above table will show that Elements 43 (masurium) and 75 (rhenium) should have many of the chemical characteristics of manganese. They would therefore be expected to possess both basic and, especially in higher stages of oxidation, acid-forming properties. From their vertical group position and from their expected electronic structure relative to their immediate horizontal neighbours, they should each show a maximum valency of 7.

	Atomic number	Electronic occupation of outer (valency) orbits		Maximum valency
		4d	5s	
Molybdenum . . .	42	5	1	6
Masurium . . .	43	6	1	7
Ruthenium . . .	44	7	1	8
		5d	6s	
Tungsten . . .	74	4	2	6
Rhenium . . .	75	5	2	7
Osmium . . .	76	6	2	8

Other properties which might have been forecast prior to their isolation include the volatility of the highest oxides (by analogy with RuO_4 and OsO_4); and they should also be capable of being precipitated as insoluble sulphides. Both of these probable properties were actually utilized in their isolation, especially in the case of rhenium.

The discovery of both of these elements is due to the work of Noddack and Tacke (afterwards Mrs. I. Noddack), with the collaboration of Berg in X-ray spectroscopic measurements. Less is known of masurium than of rhenium, with regard to which a relatively large and increasing literature exists.

MASURIUM (ELEMENT 43)

Although compounds of this element have not yet been extracted in a pure state, there seems to be no reasonable doubt of its presence in very small concentrations in many minerals (columbite, gadolinite, and sperryolith) of the same types as those which have been used as sources of rhenium: further, as would be expected, the same enrichment methods can be used successfully for both elements, save that the final separation process, involving the sublimation of a volatile highest oxide from a relatively non-volatile residue, is apparently far less effective for masurium than for rhenium. This factor probably explains the failure to prepare pure masurium salts.

The evidence for the existence of masurium depends almost entirely on what seem to be completely trustworthy X-ray spectroscopic data. Thus, the very distinct photographs, above all of the strong K_{α_1} line, published by Noddack, Tacke, and Berg† and the gradual intensification both of this line and of the weaker α_2 and β_1 lines, all in the

† W. Noddack, I. Tacke, and O. Berg, *Sitzungsber. Preuss. Akad. Wiss., Phys.-Math. Kl.* 1925, 400; *Naturwiss.* 1925, 13, 567.

calculated positions, as enrichment proceeds, seem conclusive. The degree of correspondence of the observed and the calculated wave-lengths of these lines is given in the following table.

TABLE 69
X-ray Spectrum of Element 43 (Lines in K Series)

	Wave-lengths, in \AA		
	α_1	α_2	β_1
Observed . . .	0.672	0.675	0.601
Calculated . . .	0.6734	0.6779	0.6000

The most detailed account which has been published of enrichment procedure for the concentration of masurium from a columbite source is contained in a paper by W. and I. Noddack.† An earlier and more general description of its extraction from sperryolith, columbite, and platinum ores has also been given by Tacke.‡

The enrichment process, starting from Norwegian columbite, is similar to that employed for rhenium (see later), both metals being concentrated simultaneously. Thus, 1.2 kg. of the ore was fused with caustic soda containing sodium nitrate and the melt extracted with water. The masurium and rhenium, together with niobium, tantalum, and manganese, form water-soluble salts; but much of the niobate and tantalate remains in the insoluble residue. The manganese in the aqueous extract can be largely removed by adding hydrogen peroxide; and the solution, which is coloured yellow by chromate, contains chiefly Nb, Ta, Mo, W, and almost all the masurium and rhenium, as sodium salts. This solution was first saturated with hydrogen sulphide, then acidified, and the precipitated sulphides separated. This was repeated many times, since, even after two precipitations followed by the addition of acid, much of the tungsten, platinum, and germanium remained in solution.

The final sulphide amounted to only 0.5–5.0 g. per kg. of columbite treated. In a few cases the occurrence of Element 43 in the sulphide concentrate could be detected by X-ray analysis by the appearance of the K_{α_1} line; but further treatment was usually necessary.

This additional enrichment involved the removal of further amounts of niobium and tantalum. The sulphide precipitates were treated

† W. and I. Noddack, *Metallbörse*, 1926, **16**, 2129; *Chem. News*, 1926, **133**, 241.

‡ I. Tacke, *Z. angew. Chem.* 1925, **38**, 1157.

with aqua regia and the solution filtered from the solid residue, which contained most of the acidic earths and tungsten. The filtrate, containing the masurium and rhenium, was evaporated to dryness on a water-bath and the solid reduced with hydrogen. Its weight after the reduction was 0.05 to 0.5 g. per kg. of columbite. The X-ray spectrum showed the K_{α_1} line strongly. The approximate composition of the preparation at this stage was:

	<i>Per cent.</i>
Ma	0.05 to 0.1
Re	0.05 to 0.1
Fe, Co, Ni, and Mn	60
Sn and Mo	25
W, Cu, Zn, Bi, Pb, Ge, As, Cd, and V	10
Nb, Ta, Ti, Zr, and Hf	5

Treatment with alkali removed, as the insoluble portion, most of the Fe, Co, Ni, Mn, Sn, Cu, and the acid earths. From the filtrate, the addition of hydrogen sulphide and acid precipitated further amounts of sulphides insoluble in acid, i.e. Mo, V, Pb, Pt, Ge, As, and a very little Nb and Ta, as well as the masurium and rhenium. Since the sulphides of the last two elements would be expected to be only very slightly soluble in cold ammonium sulphide, the mixed sulphides were treated with a little of this reagent in order to dissolve out the sulphides having greater solubilities in ammonium sulphide. The residue (0.002 to 0.02 g. from each kilogram of the original columbite) had an average composition:

	<i>Per cent.</i>
Ma	0.2 to 1.0
Re	1 to 5
Pb	50
Mo	30
V	10
Pt	5
Nb	2
W	1
Zn	0.5 to 2
Ta	0.1 to 0.5

This product showed up to three lines of Element 43, namely, K_{α_1} , K_{α_2} , and K_{β_1} , as well as the rhenium (Element 75) lines L_{α_1} , L_{α_2} , L_{β_1} , L_{β_2} , and L_{β_3} .

Since the masurium was not prepared in a pure state—its richest concentrates having a masurium content of only about 1 per cent.—its chemical properties, or indeed its approximate atomic weight,

could not be determined, apart from deductions as to its properties which can be made from the course of the enrichment. Inferences made in this way include, however, the confirmation of the acidic nature of what, from analogy, is probably its highest oxide, also the formation of an insoluble sulphide. As has already been mentioned, a final separation from its relatively rich concentrates by volatilizing its oxide in oxygen, which was the decisive and surprisingly successful factor in making possible the preparation of pure rhenium salts, appears not to be, at any rate so easily, applicable to masurium; and a further search for a method of separating masurium from, for instance, its 1 per cent. concentrate is undoubtedly desirable, although the work would certainly be laborious on account of the long and complicated separation process required to obtain even small quantities of such a concentrate.

It may be noted that various radioactive isotopes of masurium, including ^{99}Ma and ^{101}Ma , can be formed† from molybdenum, both by bombardment methods and by the spontaneous decay of radioactive molybdenum isotopes; and it is possible that the use of artificial masurium may involve less difficult separations than those associated with the natural element and may allow an easier study of some of its principal properties.

RHENIUM (ELEMENT 75)

The chief difficulty encountered by Noddack, Tacke, and Berg in their search for Element 75 during the period 1922–5 lay in the very small rhenium content (of the order of 10^{-6}) even of its richest natural sources. Some of the lines of its optical spark or arc spectrum, especially the triplet at 3640 Å, can, however, be seen at concentrations below 10^{-7} . These lines, which were first of all observed faintly in a number of platinum ores, were ascribed by the above workers to an, at that time, unknown metal and were correctly presumed to be due to the missing Element 75. It was found subsequently that the same lines were given by other minerals, above all by certain specimens of gadolinite, columbite, and alvite, also in general by molybdenite.

The eventual preparation of rhenium compounds in a pure state involved the development, first of all, of enrichment methods by

† G. T. Seaborg and E. Segrè, *Phys. Rev.* 1939, **55**, 808; P. H. Abelson, *ibid.* 1939, **56**, 753; R. Segane, S. Kojima, G. Miyamoto, and M. Ikawa, *ibid.* 1940, **57**, 750.

means of which these very small concentrations were increased successively up to a value (about 10^{-4}) at which the presence of Element 75 could be recognized with certainty by its X-ray spectrum—the lines in which are predictable for an element of given atomic number—and subsequently to a further and far higher stage of concentration at which the rhenium can be separated by virtue of the volatility of its highest oxide. The planning of methods of enrichment, without at the time any direct knowledge of the properties of rhenium, was based, firstly, on the probable formation of soluble salts by fusion with alkalis under oxidizing conditions, secondly, on the probable formation of an insoluble sulphide, and thirdly, on the already mentioned volatility of the oxide. For an account of the search for Element 75, reference should be made to Noddack's monograph.†

Sources of Rhenium

The platinum ores in which rhenium was recognized at an early stage have not proved of great importance for its extraction. The first appreciable quantity (120 mg.) was isolated from a gadolinite, with alvite and columbite as alternative sources. The approximate rhenium content of selected specimens of these minerals was as follows:

<i>Mineral</i>	<i>Principal constituents</i>	<i>Rhenium content</i>
Gadolinite . .	Fe, Be, Y silicate	10^{-6}
Alvite . . .	Zr, Hf silicate	5×10^{-7}
Columbite . .	Fe, Mn, Nb, Ta oxide	2×10^{-7}

Certain sulphide ores, including natural iron sulphide, copper sulphide, and, above all, molybdenum sulphide (molybdenite), the last of which had in some cases a rhenium content as high as 4×10^{-6} , were, however, found to have the advantage of requiring considerably easier separation methods; and the first gram of rhenium‡ was made from Norwegian molybdenite. It has later been extracted commercially, in amounts of many kilograms a year, from by-products obtained during the technical treatment of copper schist.

Extraction from Columbite

The method used for its extraction from columbite and similar minerals has been described by I. and W. Noddack.§ The finely

† *Das Rhenium*, publ. by L. Voss, Leipzig, 1935.

‡ I. and W. Noddack, *Z. anorg. Chem.* 1929, **183**, 353.

§ I. and W. Noddack, *Z. physikal. Chem.* 1927, **125**, 270.

ground mineral (usually in charges of 1 to 20 kg.) is fused with twice its weight of sodium hydroxide containing 5 per cent. of sodium nitrate, the melt being cooled and digested with cold water. The solution contains substantially all the rhenium, as sodium perrhenate; but the extraction should be carried out with precautions, which are given in detail in the paper, to avoid as far as possible the extraction of soluble sodium salts of niobium and tantalum. The next step consists in adding hydrogen peroxide to precipitate the manganese as the dioxide. Ammonium chloride is then added to precipitate Si, Ti, Nb, and Ta; and the solution is acidified with sulphuric acid, when a precipitate forms which contains principally Ti and Pb, together with some Si, Nb, Ta, Zr, and Hf, but no Re. Hydrogen sulphide is passed through the filtrate and the precipitated sulphides, which include the rhenium, are filtered off. This concludes the first stage in the enrichment.

The mixed sulphides are treated with aqua regia; and the solution is freed by filtration from free sulphur and undissolved matter and re-precipitated as sulphides, as before. In an example given, the metals in this second sulphide precipitate (Sulphide II) contained as much as 0.2 per cent. of rhenium, which could be clearly recognized by its X-ray spectrum. The remainder of the enrichment consisted in a complete repetition of the above procedure, including (after reduction in hydrogen) the fusion with sodium hydroxide and nitrate. Two such further repetitions gave a sulphide (Sulphide IV) which was sufficiently rich in rhenium for the final extraction of this metal as the volatile heptoxide, the sulphide being first reduced in hydrogen and afterwards heated in a current of oxygen. The extraction from gadolinite is somewhat similar.

Extraction from Molybdenite (Molybdenum Sulphide)

The Norwegian molybdenite which was used by W. and I. Noddack† for their preparation of the first gram of rhenium contained 58 per cent. of molybdenum, 39.8 per cent. of sulphur, and only 0.0002 to 0.0004 per cent. of rhenium. Traces of many other elements, including Se, Si, Al, Ca, Ti, Fe, Ni, and Co, were also present.

In order to obtain the gram of rhenium it was necessary to treat 660 kg. of the finely ground mineral. This was dissolved in batches in strong ($d = 1.4$) nitric acid, each batch consisting of 5 kg. of

† I. and W. Noddack, *Z. anorg. Chem.* 1929, **183**, 353.

molybdenite and 25 litres of acid contained in a large porcelain basin. No extraneous heating was required, since the mixture heated itself. An excess of ammonia was then added to bring the molybdenum completely into solution as ammonium molybdate. The solution was separated from any solid residue and the molybdenum partly precipitated as phosphomolybdate by means of disodium phosphate. The rhenium is not precipitated. Next, yellow ammonium sulphide was added, when a mixed precipitate of molybdenum and rhenium sulphides was obtained.

This mixed sulphide (Mo—Re I) was re-treated successively with nitric acid, ammonia, and ammonium sulphide, the whole treatment being repeated in all five times. At this stage it was convenient to remove traces of Ni, Cu, Co, Fe, etc. To this end, the total sulphide, Mo—Re V, was reduced in hydrogen at 1,000°, then fused with 300 g. of sodium hydroxide and 50 g. of sodium nitrate in a silver dish. The melt, which contained the rhenium, was dissolved in water and again precipitated with ammonium sulphide and sulphuric acid. The metal obtained by the reduction of this mixed sulphide, Mo—Re VI, with hydrogen contained 1.9 per cent. of rhenium, 68.5 per cent. of molybdenum, and 23 per cent. of vanadium, the remainder being mainly heavy metals including platinum, iridium, and lead; but about 3 per cent. of arsenic was also present. The enrichment process was then complete; and the rhenium could be separated, as Re_2O_7 , by sublimation in a current of oxygen and further purified by the same means.

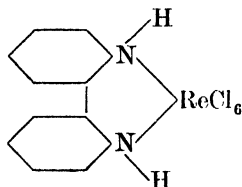
In a modified method which has been described by Kronmann, Bibikowa, and Aksenowa,† the molybdenite was also dissolved in nitric acid, but the phosphate precipitation process for removing the bulk of the molybdenum was not used. In place of this, the nitric acid solution of the mineral was evaporated to a small volume in order to precipitate as much molybdenum as possible as the trioxide. The concentrated liquid was then distilled up to 170° in a current of carbon dioxide and, from 200° onwards, in a current of gaseous hydrochloric acid. The latter distillate was reduced in volume on a water-bath and the rhenium, together with some molybdenum, precipitated with hydrogen sulphide. It was further freed from molybdenum by precipitating this with oxyquinoline;‡ and the

† E. Kronmann, V. Bibikowa, and M. Aksenowa, *Z. anorg. Chem.* 1933, **214**, 143.

‡ W. Geilmann *et al.*, *ibid.* 1930, **193**, 311; 1931, **195**, 289; **199**, 347.

rhenium was then precipitated as the difficultly soluble nitron salt (see p. 204).

This volatility of rhenium chloride in gaseous hydrochloric acid was also utilized by Morgan.[†] The main procedure was similar to that employed by Kronmann and his co-workers; but the distillation in a current of hydrochloric acid was repeated in order to obtain a further enrichment in rhenium, which distils over more rapidly than molybdenum. The final purification was, as before, carried out by treatment with 8-hydroxyquinoline, which precipitates the molybdenum, supplemented by the precipitation of the rhenium with nitron; but, as an alternative method the rhenium was precipitated, as dipyridyl rhenichloride



by adding 2, 2'-dipyridyl.

Metallic Rhenium

Rhenium is easily made by reducing its oxides or suitable salts with hydrogen: thus rhenium heptoxide, or the lower oxides, are reduced to metal at temperatures above 800°. I. and W. Noddack[‡] found, however, that it was preferable first to convert the rhenium into the sulphide and then to reduce this with hydrogen at about 1,000°; although rhenium sulphide prepared by precipitation from solution is liable to be colloidal and to include impurities. This disadvantage can be eliminated by precipitation under pressure.[§]

Probably the most satisfactory method consists in the reduction of potassium or ammonium perrhenate. The process used on a technical scale has been described by Feit,^{||} the potassium perrhenate being mixed with an excess of an alkali chloride and reduced with hydrogen at a red heat. The function of the alkali chloride is to minimize any attack on the furnace wall, by absorbing the potassium hydroxide formed from the potassium perrhenate. After the reduc-

[†] G. T. Morgan, *J. Chem. Soc.* 1935, 567.

[‡] I. and W. Noddack, *Z. anorg. Chem.* 1929, 183, 371.

[§] C. Agte, H. Alterthum, K. Becker, G. Heyne, and K. Moers, *ibid.* 1931, 196, 129.

^{||} W. Feit, *Z. angew. Chem.* 1930, 43, 459.

tion, the melt is lixiviated with water and the metallic rhenium remains as a black powder. On a small scale,† potassium perrhenate may be reduced, for instance at $1,000^{\circ}$, without the addition of an absorbing substance, since most of the potassium hydroxide produced is absorbed by the porcelain boat; and any small quantity of alkali in the metallic powder can be eliminated by washing with very dilute acetic acid. The complication of the production of alkali can moreover be completely eliminated by reducing ammonium, in place of potassium, perrhenate. This has an additional preparative advantage by reason of the difficultly soluble nature of the ammonium salt, which can consequently easily be precipitated from its concentrated solutions.

Agte and his collaborators have also described the preparation of rhenium by the thermal decomposition of gaseous rhenium chlorides on an electrically heated tungsten filament at about $1,800^{\circ}$ in a way similar to that used for making metallic hafnium; but the rhenium filament thus produced has, of course, a tungsten core.

Rhenium may be deposited electrolytically from dilute potassium perrhenate solutions containing about 5 per cent. of sulphuric acid, a suitable current density being 0.25 amp. per sq. decimetre.‡ The metal deposit is, however, stated to be impure. This was also observed by Agte. Further details of the electrodeposition of rhenium have been given by Young.§

Properties of Elementary Rhenium

The atomic weight of rhenium has been determined by Hönigschmid and Sachtleben,|| who obtained a value of 186.31 ± 0.02 on the basis of the analysis of silver perrhenate. According to Aston,¶ natural rhenium contains two isotopes, ^{185}Re and ^{187}Re , with abundances in the ratio of 1 to 1.62. This ratio leads, after considerations of packing fractions, to an atomic weight of 186.22 ± 0.07 .

Some of the principal physical properties of rhenium are given in Table 70, the values being in most cases due to Agte and his co-workers or to W. and I. Noddack.

† C. Agte *et al.*, loc. cit.

‡ G. E. F. Lundell and H. B. Knowles, *J. Research Nat. Bureau Standards*, 1937, **18**, 629.

§ C. B. F. Young, *Met. Ind.*, N.Y. 1936, **34**, 176.

|| O. Hönigschmid and R. Sachtleben, *Z. anorg. Chem.* 1930, **191**, 309.

¶ F. W. Aston, *Nature*, 1931, **127**, 591; *Proc. Roy. Soc.* 1931, A **132**, 487.

TABLE 70

Melting-point, ° Abs.	3,940±60
Specific heat	0.0346
Density	20.9
Atomic radius, in Å	1.382
Electrical resistance at 0° C.; $\rho \times 10^4$ (in Ω cm.)	0.198
Temp. coeff. of resistance between 0° and 120° C.; $\alpha \times 10^2$	0.31

In a compact state, rhenium is a silver-white metal which does not tarnish easily. The finely divided metal is, however, often pyrophoric. Although specimens sintered below its melting-point are usually rather brittle, Agte and Moers† found that rhenium prepared by the thermal decomposition of the chloride on a tungsten filament is soft and has a pliability equal to that of copper. In this state it can be bent without fracture, rolled out into a ribbon, or even drawn out into wire. The crystal structure shows hexagonal close packing,‡ with lattice constants $a = 2.765$ Å, $c = 4.470$ Å, and $c/a = 1.616$. Its coefficient of linear expansion, as measured by X-ray methods, is 12.45×10^{-6} in the direction of the hexagonal axis and 4.67×10^{-6} in a direction perpendicular to this.

Rhenium is readily oxidized by elementary oxygen at a high temperature and still more easily by fusion with alkali hydroxides in the presence of air or of oxidizing agents, alkali perrhenates being formed. It is also attacked by chlorine, less readily by bromine, and hardly at all by iodine. It dissolves easily in nitric acid, more slowly in concentrated sulphuric acid; but it is practically insoluble in hydrofluoric acid. It is not affected by mercury.

Rhenium has been used as a hydrogenation catalyst at high temperatures. It reduces§ carbon monoxide to methane at 350–400°, or ethylene to ethane at 300°, the reaction being accompanied by some decomposition and formation of by-products. The use of rhenium as a dehydrogenation catalyst has been studied particularly by Platonov and his co-workers. It is especially active for reactions such as the dehydrogenation of alcohols to aldehydes or ketones: thus, Platonov, Anisimov, and Kraschennikova state|| that rhenium on kaolin is as efficient at 400° for the dehydrogenation of ethyl alcohol to acetaldehyde, or of isopropyl alcohol to acetone, as copper

† C. Agte *et al.*, loc. cit.; see also *Naturwiss.* 1931, **19**, 108.

‡ V. M. Goldschmidt, *Z. physikal. Chem.* 1929, B **2**, 244.

§ H. Tropsch and R. Kassler, *Ber.* 1930, **63**, 2149.

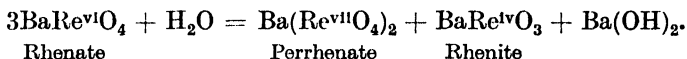
|| M. S. Platonov, S. B. Anisimov, and M. Kraschennikova, *ibid.* 1936, **69**, 1050; *J. Gen. Chem. Russ.* 1935, **5**, 1059.

at 300°; but it is stated to be less suitable for hydrogenation. It also, at 350–400°, dehydrogenates cyclohexanol to cyclohexanone;† but some phenol is also formed. The catalyst is conveniently prepared by reducing ammonium perrhenate with hydrogen‡ at 400°. It may be noted that rhenium is stated to be activated, in place of being poisoned, by hydrogen sulphide or arsenious oxide. It would thus seem to resemble molybdenum or tungsten, both of which dehydrogenate well in a sulphide form at high temperatures. In addition to these high-temperature reactions, rhenium dehydrogenates formic acid, to carbon dioxide and hydrogen, at 100–250°.

COMPOUNDS OF RHENIUM

Rhenium in its compounds may have a valency of 3, 4, 5, 6, or 7. Its characteristic valency states are, however, 4, 6, or 7, the last being in general by far the most stable. Compounds containing mono- or divalent rhenium§ have also been claimed; but less is known of these.

By reason of this large number of valency states and of differences in their stability, rhenium exhibits the phenomenon of disproportionation (spontaneous change of a given valency to a mixture of more stable valency forms) to a greater extent than is the case with any other element. An example of this effect is the disproportionation which occurs in a solution of a rhenate, particularly in the presence of acids



This is equivalent to a process: $3\text{Re}^{\text{VI}} = 2\text{Re}^{\text{VII}} + \text{Re}^{\text{IV}}$. Other instances of disproportionation are contained in the following sections.

OXIDES AND OXY-ACIDS

The three oxides ReO_2 , ReO_3 , and Re_2O_7 , corresponding with the stable valencies 4, 6, and 7, are known with certainty. There is, in addition, evidence for the existence, in a hydrated form, of a sesquioxide, Re_2O_3 ; and alkali salts (hyporhenates) derived from an oxide, Re_2O_5 , have also been reported, although the oxide itself is unknown. The two higher oxides, ReO_3 and Re_2O_7 , are anhydrides of definite

† E. V. Tur, S. B. Anisimov, and M. S. Platonov, *J. Gen. Chem. Russ.* 1937, 7, 2895.

‡ M. S. Platonov and V. I. Tomilov, *ibid.* 1937, 7, 776, 778.

§ I. and W. Noddack, *Z. anorg. Chem.* 1933, 215, 129; W. Geilmann and L. C. Hurd, *ibid.* 1933, 214, 280; G. E. F. Lundell and H. B. Holmes, *J. Research Nat. Bur. Standards*, 1937, 18, 629.

oxy-acids which form salts with metals generally. The oxide, ReO_2 , forms compounds corresponding to the manganites on being fused with alkali hydroxides.

The above range of oxides and oxy-acids, together with the heats of formation of the oxides, which provide a rough guide to the general stability of the respective valency state, is tabulated below.

TABLE 71

Valency of Re	Oxide	Colour of oxide	Heat of formation, in kg.-calcs. per mole	Corresponding oxy-acids	Formula of potassium salts
3	Re_2O_3	Black	c. 90†	—	—
4	ReO_2	Black	c. 70†	Rhenites	K_2ReO_3
5	—	—	—	Hyporhenates	KReO_3
6	ReO_3	Orange-red	82.5‡	Rhenates	K_2ReO_4
7	Re_2O_7	Yellow	299 (= 149.5 per g.-atom Re)	Perrhenates	KReO_4 (meta-perrhenate) or K_3ReO_5 (meso-perrhenate)

† W. Meidinger and W. Noddack. Unpublished, but quoted by I. and W. Noddack on pp. 63 and 70 of their monograph *Das Rhenium*.

‡ W. A. Roth and G. Becker, *Z. physikal. Chem.* 1932, A **159**, 415.

The greater heat of formation of the characteristic heptoxide agrees with the tendency of rhenium compounds of other valencies to undergo disproportionation to Re^{VII} . In addition to the above oxides, the preparation of still lower oxides, Re_2O and ReO , has been claimed. The individual oxides and oxy-acids are treated in greater detail below.

Re_2O and ReO

The preparation of both these oxides in a hydrated form, $\text{Re}_2\text{O} \cdot 2\text{H}_2\text{O}$ and $\text{ReO} \cdot \text{H}_2\text{O}$, by the reduction of perrhenic acid with zinc and with cadmium respectively has been described by Young and Irvine.§ This reduction was carried out in 0.2N hydrochloric acid solution in the absence of air, when a black deposit was formed which was afterwards washed with 12N hydrochloric acid. The residue had a composition which, in a number of tests, approximated closely to $\text{Re}_2\text{O} \cdot 2\text{H}_2\text{O}$ if zinc was used for the reduction and to $\text{ReO} \cdot \text{H}_2\text{O}$ for a corresponding reduction with cadmium. Re_2O_3 was

§ R. C. Young and J. W. Irvine, *J. Amer. Chem. Soc.* 1937, **59**, 2648.

shown to be absent. Determinations of the valency of the rhenium were made by measuring the oxygen required for conversion to Re_2O_7 . Although further work on these lower oxides appears to be required, their existence has been reported by other authors.†

Rhenium Sesquioxide, Re_2O_3

A hydrated form of this oxide has been made by Geilmann, Wrigge, and Biltz‡ by the hydrolysis of rhenium trichloride with alkali hydroxides. It is a black precipitate which readily undergoes oxidation. By working under air-free conditions, including the use of solutions of rhenium trichloride and of sodium hydroxide previously saturated with nitrogen, Geilmann and Wrigge were able to obtain precipitates in which the ratio of rhenium to oxygen varied between $\text{Re}_2\text{O}_{3.2}$ and $\text{Re}_2\text{O}_{3.4}$, the oxygen content being always slightly above that corresponding with Re_2O_3 . This was shown to be due to the capacity of Re_2O_3 to become further oxidized by slowly decomposing water with formation of hydrogen.§ This property of decomposing water is possessed by a number of lower metallic oxides.|| e.g. by W_2O_3 . Rhenium sesquioxide does not act as an acid anhydride.

Rhenium Dioxide, ReO_2 , and the Rhenites

The reduction of rhenium heptoxide leads to successive colour changes which seem to indicate a passage through lower oxides. If the reduction is carried out with hydrogen at about 300° , a black oxide is obtained¶ which has the composition ReO_2 . The same oxide is produced on gently heating ammonium perrhenate or sodium perrhenate in a current of hydrogen.

Biltz and Lehrer†† recommend the use of metallic rhenium as the reducing agent, the reaction being



The conditions for the production of the dioxide are somewhat different from those required for making the trioxide, ReO_3 (q.v.). The above workers heated a mixture of rhenium heptoxide and

† H. Holemann, *Z. anorg. Chem.* 1933, **211**, 195; W. Geilmann and L. C. Hurd, *ibid.* 1933, **214**, 260.

‡ W. Geilmann, F. W. Wrigge, and W. Biltz, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl.* 1932, 579; W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.* 1933, **214**, 239.

§ See also G. Schikorr, *ibid.* 1933, **212**, 33.

|| R. C. Young, *J. Amer. Chem. Soc.* 1932, **54**, 4515.

¶ I. and W. Noddack, *Z. anorg. Chem.* 1929, **181**, 32.

†† W. Biltz and G. A. Lehrer, *ibid.* 1933, **214**, 227.

rhenium, in the calculated stoichiometric ratio, in a silica tube to 300° for a day, when a mixture containing the red oxide (ReO_3) was formed. The temperature was then raised to 600–650° and maintained at this for a further day. The greyish-black oxide thus produced was found on analysis to correspond almost exactly with ReO_2 . It can also be made by the chemical† or electrolytic‡ reduction of solutions of perrhenates or by precipitating derivatives of the rhenium tetrahalides (e.g. K_2ReCl_6) with an alkali hydroxide.

Rhenium dioxide is not readily decomposed by heating in the absence of air; but at high temperatures it undergoes disproportionation into Re_2O_7 and metallic rhenium.

If rhenium dioxide is fused with alkalis in the absence of air, compounds analogous to the manganites and known as rhenites are obtained§ as an insoluble brown residue after extracting the melt with water:



Derivatives of Re_2O_5 : Hyporhenates

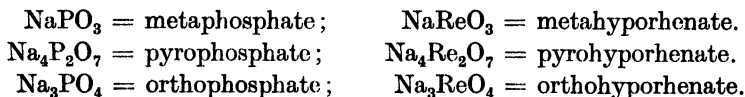
Although an oxide of pentavalent rhenium, Re_2O_5 , does not appear to exist as such, well-defined salts derived from this oxide and known as hyporhenates have been prepared|| by heating rhenium dioxide, an alkali perrhenate, and excess of an alkali for long periods to 700°. The change may be represented by the disproportionation



corresponding with



since, under these conditions, the pyrohyporhenate is produced. The nomenclature meta-, pyro-, and ortho-salts is applied by analogy with oxy-salts of other pentavalent elements, such as the phosphates, i.e.:



These alkali pyrohyporhenates, although accompanied in the melt by unchanged perrhenate (also by insoluble rhenite, formed from

† I. and W. Noddack, *Z. angew. Chem.* 1931, **44**, 215.

‡ H. Holemann, *Z. anorg. Chem.* 1931, **202**, 277.

§ I. and W. Noddack, *ibid.* 1933, **215**, 134; W. Biltz, *ibid.* 1933, **214**, 232.

|| I. and W. Noddack, *ibid.* 1933, **215**, 136.

ReO_2 and the alkali), are not very soluble and have been obtained in a pure state. The sodium salt is described as sand-yellow crystals. It is stable over long periods in strong aqueous or alcoholic alkali; but in water, ammonia, or acids it undergoes reversed disproportionation into Re^{IV} and Re^{VII} .

Rhenium Trioxide, ReO_3 , and the Rhenates

This oxide, which has a characteristic orange-red colour, is formed during the incomplete combustion of rhenium in oxygen. It was made by Biltz, Lehrer, and Meisel† by the reduction of rhenium heptoxide with rhenium; but its preparation in a pure state by this method is rendered difficult by the presence of both unchanged Re_2O_7 and metal in the melt.‡ Biltz, Lehrer, and Meisel were, however, able to obtain a red oxide which had the composition $\text{ReO}_{3.13}$ and showed, on X-ray analysis, the absence of metallic rhenium. The crystal structure was also determined.

The trioxide was subsequently prepared in a substantially pure state§ by the reaction



In this preparation, a mixture of two parts by weight of Re_2O_7 and one part of ReO_2 was heated in a silica tube for 7 days at 300° . The unattacked heptoxide was then removed by sublimation and replaced by fresh heptoxide, following which the excess was again removed.

Rhenium trioxide, on being heated to 400° in a vacuum, undergoes disproportionation into the Re^{VII} and Re^{IV} oxides. It is the anhydride of the rhenates.

The formation of green salts of a rhenium oxy-acid was observed by I. and W. Noddack,|| who noticed, during the oxidation of yellow hyporhenate-alkali melts with oxygen and before the production of red alkali mesoperrhenates, the development of a green coloration which appeared to be due to an alkali salt in which the rhenium has a valency intermediate between 5 and 7. Similar green salts were obtained by heating rhenium dioxide, sodium perrhenate, and sodium hydroxide to temperatures between 350° and 500° ; but heating to higher temperatures, e.g. to 700° , gave only hyporhenates. These

† W. Biltz, G. A. Lehrer, and K. Meisel, *Nachr. Ges. Wiss. Göttingen, Math-phys. Kl.* 1931, 191; *Z. anorg. Chem.* 1932, 207, 113, 121.

‡ H. V. A. Briscoe, P. L. Robinson, and A. I. Rudge, *J. Chem. Soc.* 1931, 3087.

§ W. Biltz and G. A. Lehrer, *Z. anorg. Chem.* 1933, 214, 225.

|| I. and W. Noddack, *ibid.* 1933, 215, 142.

green salts of hexavalent rhenium are known as rhenates and are analogous to the manganates.

Rhenates of the alkali metals are unstable in water and have not been separated in a pure form from the melt; but it has been found possible to make pure specimens of difficultly soluble rhenates, such as barium rhenate, by heating a mixture of rhenium dioxide, barium perrhenate, and sodium hydroxide for an hour at 500°, followed by a further hour at 300°. On extracting the melt with water, barium rhenate, BaReO_4 , remains as a leaf-green powder. This is washed quickly with alcohol and dried in a vacuum. It is, however, unstable; and it is quickly decomposed in solution, especially in the presence of acids, undergoing disproportionation to perrhenate and rhenium dioxide or rhenite.

Rhenium Heptoxide, Re_2O_7 , and the Perrhenates

Rhenium heptoxide, together with its oxy-acid and salts derived from this, presents no difficulty in preparation, since these are the final oxidation products in the oxidation of rhenium or its lower oxides.

The anhydrous oxide is most easily made by the direct oxidation of the metal. This oxidation takes place at 150°, but higher temperatures are ordinarily used. I. and W. Noddack† led dry oxygen over a boat containing metallic rhenium in a heated combustion tube. The volatile oxide rapidly collected as a deposit and was driven, by heating, into a receiver, in which it formed a yellow loose crystalline mass.

Rhenium heptoxide melts‡ at 304°, but has a considerable sublimation pressure below this temperature. By reason of this rapid sublimation, its boiling-point could not easily be determined. I. and W. Noddack state this to be above 350°. In the vapour state the oxide corresponds with the monomeric formula, Re_2O_7 . Rhenium heptoxide is easily soluble in water and in alcohol, but only slightly soluble in ether. Its aqueous solution is acidic.

Reducing gases such as carbon monoxide or sulphur dioxide reduce the heptoxide slowly in the cold and rapidly on warming, the production of lower oxides being accompanied by colour changes. Hydrogen at 300° reduces it to ReO_2 and, at 500°, to metallic rhenium.

† I. and W. Noddack, *Z. anorg. Chem.* 1929, **181**, 1.

‡ W. Biltz, G. A. Lehrer, and K. Meisel, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl.* 1931, 191.

Aqueous solutions of rhenium heptoxide contain the strong acid, HReO_4 , and dissolve many metallic hydroxides, including the hydroxides of zinc and iron. They also dissolve metallic iron or zinc with evolution of hydrogen. Addition of ammonium sulphide or passage of hydrogen sulphide through a solution of perrhenic acid or its salts, even in dilute hydrochloric acid, precipitates the sulphide. Nascent hydrogen reduces perrhenates to rhenates. Hydrogen peroxide has no action on aqueous perrhenates (see however p. 190).

The perrhenates fall into two classes, corresponding with ordinary (meta) perrhenic acid, HReO_4 , and with an acid at a further stage of hydration, mesoperrhenic acid, H_3ReO_5 . The alkali perrhenates are readily made by the neutralization of perrhenic acid. NaReO_4 melts at about 300° , KReO_4 at about 350° . Their solubility,† in moles per litre, is as follows. For comparison, the solubilities of the corresponding perchlorates, which they resemble, are included in the table. The low solubility of potassium, compared with sodium perrhenate should be noted.

TABLE 72

<i>Salt</i>	<i>Solubility of</i>	
	<i>Perrhenate</i> (all at 19°)	<i>Perchlorate</i>
Na . . .	3.5	17.28 at 25°
K . . .	0.034	0.121 at 20°
Rb. . .	0.031	0.055 at 20°
Cs . . .	0.020	0.070 at 20°
NH_4 . . .	0.227	2.136 at 25°

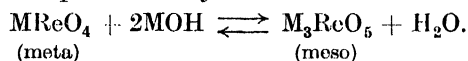
Silver perrhenate is precipitated on adding silver nitrate to a neutral solution of sodium or potassium perrhenate. It has a solubility of 3.2 g. per litre and is stated to be easily obtained pure. Barium perrhenate was made by Noddack and Noddack by neutralizing the acid with baryta. It consists of white needles which are fairly soluble in water (150 g. per litre).

While the ordinary perrhenates of the alkalis or alkaline earths are colourless, yellow melts which are red when hot and which still contain rhenium in the seventh-valency state are obtained by fusing, for instance, sodium perrhenate with sodium hydroxide.‡ This yellow

† E. Wilke and T. Gunzert, *Z. anorg. Chem.* 1933, **215**, 369.

‡ I. and W. Noddack, *ibid.*, p. 145.

coloration has been shown to be due to the presence of salts of a polybasic perrhenic acid, mesoperrhenic acid, H_3ReO_5 . The terminology meta- and mesoperrhenic acid was adopted by Noddack in view of some similarity of heptavalent rhenium, in the perrhenates, to heptavalent iodine in the iodates. The yellow colour disappears on dissolving the alkali melts in water; but barium mesoperrhenate has been prepared in a pure state both by fusion and in solution (see below). The passage of meta- into mesoperrhenates, and its reversal, may be represented by



I. and W. Noddack prepared barium mesoperrhenate by fusing barium metaperrhenate with carbonate-free sodium hydroxide. It was also made by Scharnow† by evaporating an aqueous solution of barium metaperrhenate with an excess of baryta water in the absence of atmospheric carbon dioxide, when a heavy yellow precipitate of barium mesoperrhenate separates out. The salt, after being dried with alcohol, is fairly stable in dry air. Water, if free from carbon dioxide, causes only a slow reversion to the meta form; but the change occurs rapidly in the presence of acids, including carbonic acid. In alkaline solution, equilibrium mixtures of meta- and mesoperrhenates, as in the above equation, are formed.

It may be noted that there is some evidence for the existence either of a peroxide higher than Re_2O_7 or of a corresponding higher peracid. Hagen and Sieverts‡ state that if a drop of perhydrol is added to solid rhenium heptoxide a deep red coloration results, which disappears on adding more water. The per-substance is accordingly only stable in the absence of an excess of water. It is also produced by adding much strong sulphuric acid to an aqueous solution of hydrogen peroxide and perrhenic acid.

The coloured substance thus formed is stable for some days at room temperature. It is soluble in ether and in alcohol, but insoluble in benzene, cyclohexane, paraffins, acetone, and chloroform. Its constitution has not been determined.

RHENIUM SULPHIDES AND SELENIDES

Two sulphides, ReS_2 and Re_2S_7 , corresponding with the stable oxides, ReO_2 and Re_2O_7 , are known. The existence of these two

† B. Scharnow, *Z. anorg. Chem.* 1933, **215**, 185.

‡ H. Hagen and A. Sieverts, *ibid.* 1932, **208**, 267.

sulphides only might have been inferred from the relationship of rhenium to its horizontal periodic neighbours, tungsten and osmium, both of which form a disulphide and a higher sulphide corresponding with the maximum valency of the group:

Group		
VI	VII	VIII
WS ₂	ReS ₂	OsS ₂
WS ₃	Re ₂ S ₇	OsS ₄

Unlike the oxides, the disulphide of rhenium is the more stable form. The selenides are very similar to the sulphides.

Rhenium Disulphide, ReS₂

This sulphide has been prepared by heating the heptasulphide to 600° in a current of nitrogen or in a vacuum, when the excess of sulphur distils off, leaving a black powder† which has a composition ReS₂. It has also been made by heating rhenium to a red heat with an excess of sulphur in a Rose crucible in an atmosphere of hydrogen sulphide;‡ or from the calculated quantities of metal and sulphur in a sealed silica tube§ which was heated for 18 hours to 1,000°.

It is a very stable substance, which has an appreciable vapour pressure at temperatures above 1,000° and sublimes unchanged. Juza and Biltz give the vapour pressure as 13 mm. at 1,110°, 55 mm. at 1,189°, and 96 mm. at 1,225° C. The sublimed sulphide is deposited in microscopic leaflets. The crystal structure has been examined by Meisel.|| Its heat of formation, from solid rhenium and gaseous sulphur, has been calculated to be 70.5 kg.-cals.

Rhenium Heptasulphide, Re₂S₇

The heptasulphide¶ is precipitated in a hydrated form by passing hydrogen sulphide through an acidic solution of a perrhenate. The precipitate does not, however, always correspond exactly with a composition Re₂S₇: thus Biltz and Weibke report compositions varying

† I. and W. Noddack, *Z. Elektrochem.* 1928, **34**, 627; *Ber.* 1930, **63**, 16.

‡ H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J. Chem. Soc.* 1931, 1439.

§ R. Juza and W. Biltz, *Z. Elektrochem.* 1931, **37**, 498.

|| K. Meisel, *Z. angew. Chem.* 1931, **44**, 243.

¶ I. and W. Noddack, *ibid.* 1931, **44**, 215; H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *loc. cit.*; W. Biltz and F. Weibke, *Z. anorg. Chem.* 1931, **203**, 3.

between $\text{Re}_2\text{S}_{6.9}$ and $\text{Re}_2\text{S}_{7.3}$. If the precipitation is carried out in ammoniacal solution, the sulphide is produced in a semi-colloidal state; but subsequent acidification with hydrochloric acid converts it into a form which is fairly easy to filter, although under these conditions the precipitation is never quantitative. It is precipitated quantitatively by boiling potassium perrhenate with an excess of sodium thiosulphate solution in the presence of acids. This sulphide cannot be made by direct synthesis.

The precipitated sulphide may be dehydrated without loss of sulphur by being heated in a high vacuum over phosphorus pentoxide, first to 140° and then for a longer period (60 hours) to 160 – 170° . At higher temperatures it loses sulphur and passes into the disulphide. The density of the dehydrated sulphide is 4.866 at 25° .

Rhenium Selenides

Both ReSe_2 and Re_2Se_7 have been made by Briscoe, Robinson, and Stoddart by methods analogous to those used for the sulphides, namely, by passing hydrogen selenide through a solution of potassium perrhenate containing potassium hydroxide to dissolve any liberated selenium. The precipitate, after being washed and dried over phosphorus pentoxide, had a composition approximating to Re_2Se_7 . On being heated in a vacuum to 325 – 330° for 9 hours, selenium was lost and the diselenide, ReSe_2 , remained. This compound appears to be very stable in air and is not easily attacked, except by strong oxidizing acids.

THIOPERRHENATES

The oxygen in perrhenic acid may be partly or completely replaced by sulphur, giving the thioperrhenates. Of these, the monothio compounds, derived from HReO_3S , are the best known.† The thallium salt, TlReO_3S , which is difficultly soluble in water (0.12 g. per 100 c.c. at 20°) was made by passing hydrogen sulphide through a cold saturated solution of potassium perrhenate for 2 days, then, after standing, for a further 2 days. The rhenium sulphide was filtered off; and, on adding thallium nitrate to the filtrate, the monothioperrhenate was precipitated as yellow needles. The alkali salts, including ammonium monothioperrhenate, are all known. By very

† W. Feit, *Z. angew. Chem.* 1931, **44**, 65; *Z. anorg. Chem.* 1931, **199**, 262; H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J. Chem. Soc.* 1932, 2811.

prolonged passage of hydrogen sulphide through neutral perrhenate solutions, progressive further substitution of sulphur for oxygen occurs; and it appears that, in alkaline solution, products derived from HReS_4 may be obtained directly,[†] without the intermediate formation of monothio compounds.

RHENIUM HALIDES AND OXYHALIDES

The failure of rhenium to form simple heptahalides, corresponding with its most stable valency state in its oxides, is probably due to steric factors, namely, to the difficulty in accommodating seven halogen atoms around a central rhenium atom at distances sufficiently short to make possible the utilization of suitable orbitals for the formation of strong bonds. This difficulty does not arise in the accommodation of, for instance, seven divalent oxygen or sulphur atoms around two (in place of one) rhenium atom, as in Re_2O_7 or Re_2S_7 , or in the obviously heptavalent oxyhalides such as ReO_3F or ReO_3Cl ; but analogous packing difficulties occur in halides of other elements of high valency, e.g. in the ion $(\text{ZrF}_7)^{3-}$, in which the seventh fluorine atom can only be accommodated by distortion,[‡] or in the non-existence§ of $(\text{MoCl}_8)^{4-}$, which Pauling also ascribes to steric hindrance, although $[\text{Mo}(\text{CN})_8]^{4-}$ exists. Further, rhenium hexafluoride, ReF_6 , is the only known hexahalide, the highest chloride being ReCl_5 , and the highest bromide ReBr_3 , although derivatives of ReBr_4 exist. This may possibly also have some steric background involving the smaller covalent radius (0.64 Å) of fluorine compared with that of chlorine (0.99 Å) and bromine (1.14 Å); but, in general, the affinity of rhenium for the halogens appears to decrease as the halogen series is ascended: thus no stable iodides of rhenium have been prepared, although derivatives exist containing ReI_4 , these being comparable with similar compounds derived from the unstable halides ReCl_4 or ReBr_4 .

The stable highest halides have the usual property of losing two halogen atoms on being heated or partly reduced. In this way ReF_6 passes into ReF_4 and ReCl_5 into ReCl_3 ; but no halides below ReX_3 (or ReF_4 in the case of the fluorides) are known.

The various halides and the better-known oxyfluorides and

[†] See I. and W. Noddack, *Das Rhenium*, pp. 54–7.

[‡] See Chapter I, p. 65.

§ Pauling, *Nature of the Chemical Bond*, p. 238.

oxychlorides of rhenium are summarized in Table 73. The formulae of compounds, the existence of which has been questioned, or which are known only in the form of derivatives, are enclosed in brackets.

TABLE 73

Valency of Re	Halides				Oxyhalides	
	F	Cl	Br	I	F	Cl
III	—	ReCl ₃	ReBr ₃	—	—	—
IV	ReF ₄	(ReCl ₄)	(ReBr ₄)	(ReI ₄)	ReOF ₂	—
V	—	ReCl ₅	—	—	—	—
VI	ReF ₆	—	—	—	{ ReOF ₄ ReO ₂ F ₂	ReOCl ₄
VII	—	—	—	—	ReO ₃ F	ReO ₃ Cl

RHENIUM FLUORIDES

Rhenium Tetrafluoride, ReF₄

Rhenium tetrafluoride is formed in small quantities by the direct action of fluorine on rhenium at a low pressure; but it is best prepared by reducing ReF₆ with hydrogen at 200° or with sulphur dioxide at 380–400°. In an apparatus described by Ruff and Kwasnik† the hexafluoride was vaporized in a current of hydrogen or sulphur dioxide diluted with oxygen-free nitrogen and the mixture was led through a heated platinum tube in which the tetrafluoride condensed in a liquid form and from which it could be knocked out as a solid after cooling. Reduction temperatures above those given led to the metal in place of to the tetrafluoride. Purification of the ReF₄ can be carried out by further distillation in platinum, since it attacks silica at temperatures above 80°. Both solid and liquid ReF₄ are dark green in colour. It melts at 124.5° and has a density of 5.383 at 26°.

It may be noted that rhenium tetrafluoride, like the other tetrahalides of rhenium, forms coordination compounds which are reminiscent of those formed by PtCl₄. Thus potassium hexafluororhenate, K₂ReF₆, has been made directly by reducing potassium perrhenate with hydriodic acid in hydrofluoric acid solution.‡ The salt crystallizes in green octahedra and dissolves in water without apparent hydrolysis. It yields Re(OH)₄ on addition of dilute alkali.

† O. Ruff and W. Kwasnik, *Z. anorg. Chem.* 1934, **219**, 77.

‡ I. and W. Noddack, *ibid.* 1933, **215**, 153; O. Ruff and W. Kwasnik, *loc. cit.*

Rhenium Hexafluoride, ReF₆

This fluoride has been prepared by passing a stream of oxygen-free fluorine over metallic rhenium,† preferably contained in a fluor-spar boat. It readily attacks any silica parts of the apparatus, forming the oxyfluoride, ReOF₄; but, by working at a low fluorine pressure (20–35 mm.), it is possible to reduce the time of contact sufficiently to minimize this reaction, substantially pure ReF₆ being obtained in a condenser cooled with liquid air.

Rhenium hexafluoride is a pale yellow volatile solid, melting at 18.8° and boiling at 47.6°. The density of the solid at 0° is given as > 4.251. The liquid has a density of 3.616 at its solidification point and 3.371 at its boiling-point. As has already been stated, it is reduced to the tetrafluoride by hydrogen or sulphur dioxide. This reduction can also be carried out with carbon monoxide or with metallic rhenium. Oxygen and oxidizing agents react with it to form ReOF₄ and possibly also ReO₃F. The reactivity of rhenium hexafluoride towards silica is so great that, at temperatures below 30°, bubbles of silicon tetrafluoride are evolved from ReF₆ in silica vessels. The product is ReOF₄.

Efforts to make the heptavalent fluoride, ReF₇, failed. Ruff and Kwasnik ascribe this to steric hindrance in the placing of seven fluorine atoms around the central rhenium atom, as has already been discussed.

RHENIUM OXYFLUORIDES

Two oxyfluorides, ReOF₄ and ReO₂F₂, derived from ReF₆, have been described by Ruff and Kwasnik. In addition, other oxyfluorides, ReOF₂ (derived from ReF₄) and ReO₃F, are known.

ReOF₄ is formed, mixed with ReF₆, if fluorine containing oxygen is led over rhenium powder at 125–300°. It is also produced if rhenium hexafluoride is allowed to remain in contact with silica at room temperature, when the oxyfluoride separates out in white crystals from the yellow liquid. It was purified by fractional distillation and repeated fractional sublimation, the oxyfluoride being obtained in the least volatile fraction.

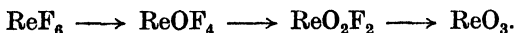
In a pure state, ReOF₄ is snow-white; but it is often coloured yellow by ReF₆. It melts at 39.7°. Its boiling-point, 62.7°, was

† O. Ruff and W. Kwasnik, *ibid.* 1932, 209, 113; 1934, 219, 65.

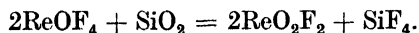
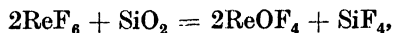
calculated by extrapolation from the vapour-pressure curve. The density of the liquid is 3.717 at its solidification point.

The chemical properties of ReOF_4 are very similar to those of ReF_6 . It reacts violently with metals such as zinc, magnesium, or aluminium but, unlike the hexafluoride, it is not very readily attacked by oxidizing agents. With alkalis, the Re^{VI} undergoes disproportionation and Re(OH)_4 is produced.

The second Re^{VI} oxyfluoride, ReO_2F_2 , occurs in small quantities, usually of the order of 5 per cent., in the reaction product obtained by heating rhenium in fluorine containing oxygen. It will be seen that this compound represents a further stage in the exchange of two atoms of fluorine for one atom of oxygen in the oxidation series



This progressive removal of fluorine can also be brought about by the action of silica,



The use of this method for the production of ReOF_4 has already been mentioned; but the product obtained by allowing ReF_6 or ReOF_4 to remain for several weeks in silica vessels always contains a considerable quantity of ReO_2F_2 , which can be purified by being heated to 90° in a high vacuum, when the ReF_6 and ReOF_4 distil off, leaving a residue of ReO_2F_2 . It melts at 156° , with decomposition, and is hydrolysed by moist air.

RHENIUM CHLORIDES

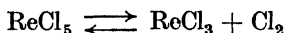
Two chlorides, ReCl_3 (green) and ReCl_5 (brown), are known with certainty and have been obtained in a pure state. An intermediate chloride, ReCl_4 , was reported by Briscoe, Robinson, and Stoddart† to be formed by the action of chlorine on metallic rhenium at about 250° ; but doubt has been thrown on this by Geilmann, Wrigge, and Biltz,‡ who have published evidence which seems to show that the principal product of the chlorination of rhenium is ReCl_5 . ReCl_4 , however, certainly exists in the form of derivatives such as K_2ReCl_6 , which is analogous to K_2PtCl_6 .

† H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J. Chem. Soc.* 1931, 2263.

‡ W. Geilmann, F. W. Wrigge, and W. Biltz, *Z. anorg. Chem.* 1933, 214, 244.

Rhenium Trichloride, ReCl₃

ReCl₃ has been made† by heating ReCl₅ in a current of dry nitrogen, when a thermal dissociation represented by



occurs. By repeatedly subliming the product along an apparatus consisting of a series of glass bulbs, a solid residue was obtained which corresponded well with a composition ReCl₃. On the other hand, if ReCl₃ was sublimed in chlorine, ReCl₅ was formed. The vapour of ReCl₃ is green, whereas that of ReCl₅ is brown.

Rhenium trichloride is reduced by hydrogen at 250–300° with production of rhenium. When dissolved in glacial acetic acid,‡ it exists in the bimolecular state, Re₂Cl₆. Its freshly prepared aqueous solution does not give a precipitate of silver chloride with silver nitrate and has only a low conductivity: hence it is apparently not ionized to any large extent. However, on standing in the cold or more quickly if the solution is heated, hydrolysis occurs with production of a black hydroxide and free hydrochloric acid, the green colour of the trichloride gradually disappearing. It is more stable in acid solution; and oxygen can be passed for a considerable time through its solution in dilute sulphuric acid without destroying the trivalency of the rhenium. This resistance to oxidation should be contrasted with the easy oxidizability of the trioxide.

Chlororhenous Acid and the Chlororhenites

Solutions of rhenium trichloride in dilute hydrochloric acid have been shown by Wrigge and Biltz to contain chlororhenous acid, HReCl₄. This acid forms a series of well-defined salts: thus, on adding rubidium chloride to a not too dilute solution of ReCl₃ in hydrochloric acid,§ the rubidium salt, RbReCl₄, is at once precipitated. In other cases it is necessary to concentrate by evaporation before crystals of the salt are obtained. The potassium salt is fairly soluble; but both this and the ammonium salt crystallize well. In general, this series of salts is less stable than the rhenichlorides, which are derived from H₂ReCl₆; and they pass, by disproportionation and deposition of rhenium, into this more stable series on being heated.

† W. Geilmann, F. W. Wrigge, and W. Biltz, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl.*, 1932, p. 579; *Z. anorg. Chem.* 1933, **214**, 248; *Z. angew. Chem.* 1933, **46**, 223.

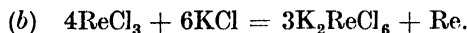
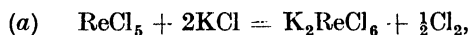
‡ F. W. Wrigge and W. Biltz, *Z. anorg. Chem.* 1936, **228**, 372.

§ W. Geilmann and F. W. Wrigge, *ibid.* 1937, **231**, 66.

Derivatives of Rhenium Tetrachloride, ReCl₄

Briscoe, Robinson, and Stoddart† prepared potassium rhenichloride, K₂ReCl₆, by heating a mixture of potassium chloride and metallic rhenium, in the calculated ratio, in a current of chlorine until the powder melted to yellowish-brown globules. A solution of this product, on being concentrated in a desiccator, yielded green crystals having the above composition. The evaporation must, according to these authors, be carried out in the cold, since decomposition begins at about 25°, with formation of a dark colloidal solution. The dried crystals are, however, stable in air and are not dissociated when heated to 300°.

It is of great interest to note that the same compound, containing Re^{iv}, was obtained by Geilmann and Wrigge both from pure ReCl₅ and from pure ReCl₃. Thus,‡ on heating ReCl₅ with the calculated quantity of potassium chloride, chlorine is evolved and K₂ReCl₆ can be crystallized from a solution of the product in dilute hydrochloric acid. On the other hand, if dry ReCl₃, in place of ReCl₅, is heated with dry potassium chloride, metallic rhenium is liberated, with formation of the same rhenichloride as was obtained from ReCl₅, the reaction courses being



This strong tendency towards the formation of K₂ReCl₆ both from ReCl₃ and from ReCl₅ suggests a possible partial reconciliation of the views of Briscoe, Robinson, and Stoddart and of Geilmann, Wrigge, and Biltz with regard to the nature of the product originally formed by the chlorination of rhenium, in that this (particularly when prepared at 250°) may actually contain some free ReCl₄ by virtue of a disproportionation equilibrium, $2\text{Re}^{\text{iv}} \rightleftharpoons \text{Re}^{\text{v}} + \text{Re}^{\text{iii}}$, corresponding with



but this product is certainly not pure ReCl₄, as was originally claimed. Even if any ReCl₄ exists in it as such it seems to be broken up on subjecting the product to sublimation: further, Geilmann, Wrigge, and Biltz were unable to obtain any evidence for free ReCl₄ or for its re-formation under any conditions, apart from the formation of K₂ReCl₆.

† H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J. Chem. Soc.* 1931, 2263.

‡ W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.* 1933, 214, 255.

Potassium rhenichloride may conveniently be prepared† by reducing potassium perrhenate with potassium iodide and fuming hydrochloric acid, the reaction being



Enk gives the following details. One gram of potassium perrhenate and 2 g. of potassium iodide, both previously finely powdered, are heated with concentrated hydrochloric acid on a sand bath until all the iodine is volatilized. The yellow reaction product is crystallized from 10 per cent. hydrochloric acid, when yellowish-green crystals of K_2ReCl_6 are obtained. According to I. and W. Noddack,‡ the first product of this reaction is an oxy-salt, $\text{K}_4\text{Re}_2\text{OCl}_{10}$, which can be isolated and which, on further reduction, passes into K_2ReCl_6 . A still further reduction, to potassium rhenium chlorides derived from rhenium having a valency less than 4, has been claimed by Krauss and Steinfeld§ and by Manchot, Schmid, and Düsing|| both for intensive reduction by Enk's method and for electrolytic reduction or reduction with zinc; but I. and W. Noddack were not able to confirm this, at any rate for reduction with hydriodic acid. I. and W. Noddack also showed that the acid, H_2ReCl_6 , can be made by boiling ReO_2 with concentrated hydrochloric acid.

The rhenichlorides (which are sometimes called the chlororhenates from their analogy to the chloroplatinates) of a number of other metals have been prepared, by precipitation, from a solution of the potassium salt. Thus, silver nitrate gives an orange precipitate of silver rhenichloride, Ag_2ReCl_6 , which is rather unstable and easily oxidized. Caesium rhenichloride, which is very stable and only very slightly soluble, is obtained similarly as a yellow precipitate. Mercurous rhenichloride is also light yellow in colour. Thallous rhenichloride, Tl_2ReCl_6 , is preferably precipitated in acetic acid solution on account of the low solubility of thallous salts (as a precipitating solution) in water.

Rhenium Pentachloride, ReCl_5

This appears to be the highest chloride; and, according to Geilmann, Wrigge, and Biltz, the product obtained by passing chlorine

† E. Enk, *Ber.* 1931, **64**, 791; I. and W. Noddack, *Z. angew. Chem.* 1931, **44**, 215.

‡ I. and W. Noddack, *Z. anorg. Chem.* 1933, **215**, 129.

§ F. Krauss and H. Steinfeld, *Ber.* 1931, **64**, 2552.

|| W. Manchot, H. Schmid, and I. Düsing, *ibid.*, p. 2905.

over metallic rhenium at 500° consists principally of the pentachloride. It was prepared in a pure state by subjecting the crude chlorination product to repeated fractional sublimation in a vacuum at 20–50°, when it can easily be separated from the less volatile trichloride and from the far more volatile oxychloride, ReOCl_4 , which are also present.

Rhenium pentachloride is dark brown or almost black: its vapour is also dark brown (cf. ReCl_3). It cannot be sublimed at atmospheric pressure without decomposition; and some decomposition also appears to occur on raising it to its melting-point. The above workers showed that this decomposition corresponds with a thermal dissociation, $\text{ReCl}_5 \rightleftharpoons \text{ReCl}_3 + \text{Cl}_2$. When the pentachloride is brought into contact with aqueous alkalis, disproportionation into Re^{vii} and Re^{iv} takes place with formation of perrhenate and of hydrated ReO_2 . In water or in aqueous hydrochloric acid, the same type of reaction occurs with formation also of free chlorine and of H_2ReCl_6 , which can be identified by adding potassium chloride and crystallizing out the K_2ReCl_6 .

Rhenium Oxychlorides

Two oxychlorides, ReOCl_4 and ReO_3Cl , derived respectively from Re^{vi} and Re^{vii} , have been made by the oxidation of rhenium trichloride. They are well-defined compounds having the following characteristics:

	<i>Colour</i>	<i>Melting-point</i>	<i>Boiling-point</i>
ReOCl_4 . . .	Brown	29·3°	223°
ReO_3Cl . . .	Colourless	4·5°	131°

Details of the preparation of both of these have been given by Geilmann and Wrigge.† The rhenium trichloride, contained in a porcelain boat, was heated in a current of air or oxygen. Oxidation, accompanied by incandescence, occurred at about 400° with evolution of a green vapour. The product was condensed in a series of receivers maintained at various temperatures, the last receiver being cooled in alcohol and solid carbon dioxide. On subjecting the raw oxidation product to fractionation in an atmosphere of nitrogen, the pure oxychlorides were obtained. One of these (ReOCl_4), which

† W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.* 1933, **214**, 250.

solidified to brown needles, occurred in the 150–200° fraction: the other (ReO_3Cl), which was extracted from the crude fraction boiling below 100°, was colourless, or slightly green when impure, and solidified at 3–4° to colourless needles. On further purification these oxychlorides had the melting- and boiling-points given in the comparative table.

The same oxychlorides had previously been made by Brukl and Ziegler,[†] both by heating rhenium chloride in oxygen and by gently heating a mixture of rhenium chloride with an excess of rhenium heptoxide. The rhenium chloride used by these earlier workers was the crude chloride obtained by chlorinating metallic rhenium.

Salts containing Rhenium, Chlorine, and Oxygen

A number of complex salts of this type have been described. Thus, in addition to the salt, $\text{K}_4\text{Re}_2\text{OCl}_{10}$, which occurs as a precursor to K_2ReCl_6 in the reduction of perrhenates with hydriodic acid, I. and W. Noddack[‡] were able to obtain a salt, K_2ReOCl_6 , by the interaction of the oxychloride, ReOCl_4 , with potassium chloride dissolved in 15 per cent. hydrochloric acid. Other complex salts have been reported by Jakob and Jezowska.[§]

RHENIUM BROMIDES

Rhenium tribromide appears to be the only bromide which has been made in the free state; but stable derivatives of the tetrabromide exist, corresponding with those derived from the tetrachloride.

Rhenium Tribromide, ReBr_3

This was prepared by Hagen and Sieverts^{||} by passing a current of nitrogen saturated with bromine over metallic rhenium at 450° in the complete absence of air or oxygen, when a sublimate of greenish-black crystals of ReBr_3 was obtained in the cooler part of the tube. If oxygen is present, a deep blue distillate is also formed, which probably contains oxybromides; but it was not found possible to isolate these in a pure state. Rhenium tribromide has also been made

[†] A. Brukl and K. Ziegler, *Ber.* 1932, **65**, 916.

[‡] I. and W. Noddack, *Z. anorg. Chem.* 1933, **215**, 180.

[§] W. F. Jakob and B. Jezowska, *Ber.* 1933, **66**, 461; see, however, I. and W. Noddack, loc. cit., p. 161.

^{||} H. Hagen and A. Sieverts, *Z. anorg. Chem.* 1933, **215**, 111.

by I. and W. Noddack† by heating rhenium with bromine in a sealed silica tube at 600°.

Rhenium tribromide is very stable and can be sublimed without decomposition at 500° in nitrogen or in a vacuum. Its vapour is dark yellow with a green tinge. It dissolves in hydrobromic acid to give a reddish-brown solution which probably contains HReBr_4 . Metallic salts of this acid were not prepared by the above authors; but the addition of pyridine precipitates a salt, $\text{C}_5\text{H}_5\text{NH} \cdot \text{ReBr}_4$.

Derivatives of Rhenium Tetrabromide, ReBr_4

The rhenibromides are very similar to the rhenichlorides. I. and W. Noddack‡ obtained a solution containing the free acid, H_2ReBr_6 , by boiling rhenium dioxide with fuming hydrobromic acid. H_2ReBr_6 , on the basis of conductivity measurements, is a weak acid like H_2ReCl_6 . On adding potassium, rubidium, or caesium salts to its solution, the corresponding rhenibromides, M_2ReBr_6 , separated as red crystalline precipitates. Difficultly soluble rhenibromides of pyridine and of nitron were also obtained.

Krauss and Steinfeld§ made potassium rhenibromide (which, however, they describe as deep violet crystals) by treating a concentrated aqueous solution of potassium perrhenate with potassium bromide and hydrobromic acid. The thallium salt was made by heating thallium perrhenate with concentrated ($d = 1.75$) hydrobromic acid.

The alkali rhenibromides dissolve in water to give yellow solutions, which are stable in the cold but undergo hydrolysis on being boiled. Solutions containing more than 15 per cent. of free HBr are stated to be completely stable. Thallous rhenibromide is soluble with difficulty in water and in dilute acids but is easily soluble in hot concentrated hydrochloric acid.

RHENIUM AND IODINE

No free iodide of rhenium has been prepared; but, as with the chlorides and bromides, stable derivatives of ReI_4 exist in the form of the rheni-iodides.

Potassium rheni-iodide was made by Briscoe, Robinson, and Rudge|| by heating potassium perrhenate, potassium iodide, and an excess of aqueous ($d = 1.7$) hydriodic acid. On cooling, crystals

† I. and W. Noddack, *Z. anorg. Chem.* 1935, 215, 177.

‡ I. and W. Noddack, *ibid.*, p. 168.

§ *Loc. cit.*

|| H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *J. Chem. Soc.* 1931, 3218.

having the composition K_2ReI_6 were deposited. These were in some cases recrystallized from acetone. The salt could be dried at 100° without decomposition; but at 300° , in a current of nitrogen, it decomposed into potassium iodide, rhenium, and free iodine. Thallium rheni-iodide has been obtained by Krauss and Steinfeld by heating thallium perrhenate with concentrated hydriodic acid.

RHENIUM COMPOUNDS CONTAINING CARBON

Very few simple compounds containing rhenium and carbon appear to have been investigated apart from firstly, the use of organic bases for the formation of salts of perrhenic and other rhenium acids and, secondly, the formation of a number of coordination compounds containing rhenium. Among the simpler carbon compounds, the following may be mentioned.

Rhenium Carbide

Rhenium does not form a carbide easily; and, on heating the ordinary form of the metal in methane or in carbon monoxide, only a little carbon is incorporated into the lattice without carbide formation.† However, if the rhenium is prepared in a specially active state, by reducing ammonium perrhenate with dry hydrogen at a temperature which is gradually raised from 200° upwards, a new phase, which was identified as a carbide, is produced by acting on this metal with carbon monoxide at 470 – 600° . This carbide is unstable and is completely decomposed at $1,600^\circ$.

Rhenium Ethoxide and Propoxide

Rhenium tri-ethoxide, $Re(OC_2H_5)_3$, and the corresponding isopropoxide, $Re(OC_3H_7)_3$, have been made by Druce‡ by the interaction of rhenium trichloride with a water-free alcoholic solution of sodium ethoxide or iso-propoxide. They are brown solids which are stable in dry air. Alcoholates such as $ReCl_3 \cdot C_2H_5OH$ also exist.

Rhenium Thiocyanates

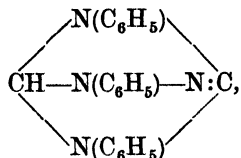
Complex coloured thiocyanates are produced on adding an alkali thiocyanate to a perrhenate. This reaction is considered further in the next section.

† W. Trzebiatowski, *Z. anorg. Chem.* 1937, **233**, 376.

‡ J. G. F. Druce, *J. Chem. Soc.* 1937, 1407.

QUANTITATIVE ESTIMATION OF RHENIUM

The organic base nitron,† which has the constitution



forms a difficultly soluble perrhenate; and rhenium is commonly precipitated in this form. According to the directions of Geilmann and Voigt,‡ a neutral solution of the perrhenate, which should contain not more than 0.1 g. of rhenium, is diluted with hot water to 50 c.c. and, after the addition of 1 c.c. of 2N-sulphuric acid, is heated to 80°. The rhenium is then precipitated by adding a slight excess of nitron acetate. After cooling to room temperature the system is further cooled for 2 hours in ice water with frequent stirring. It is then filtered through a filter cone previously dried at 110°, the precipitate being washed with 10–20 c.c. of 0.3 per cent. aqueous nitron acetate, followed by 2–3 c.c. of ice-cold water previously saturated with nitron perrhenate. Finally, the precipitate is dried at 110°. Its rhenium content is obtained by multiplying by the factor 0.3306. The solubility of nitron perrhenate in water is 0.017–0.018 g. per 100 c.c. at 0°; and it is practically completely insoluble in 0.3–0.5 per cent. nitron acetate solution.

The above simple precipitation method cannot be used if nitric acid or halogen acids are present. In this case the rhenium is first precipitated as the sulphide, which, after separation, is oxidized to perrhenic acid with hydrogen peroxide,§ and then precipitated as the nitron salt. This procedure may be used for the estimation of rhenium in the presence of other metals which are precipitated as sulphides, e.g. Cu, Pb, Hg, As, Sb, and Sn.

Rhenium cannot conveniently be weighed as the sulphide. Its estimation by precipitation as the dioxide|| has been criticized by Geilmann and Hurd¶ on account of the easy further oxidation of this oxide. This causes changes in the oxygen content of the precipi-

† M. Busch, *Ber.* 1905, **38**, 856.

‡ W. Geilmann and A. Voigt, *Z. anorg. Chem.* 1930, **193**, 311.

§ W. Geilmann and F. Weibke, *ibid.* 1931, **195**, 289.

|| I. and W. Noddack, *Z. angew. Chem.* 1931, **44**, 215; H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J. Chem. Soc.* 1931, 665.

¶ W. Geilmann and L. C. Hurd, *Z. anorg. Chem.* 1933, **214**, 260.

tate and leads to losses during washing. For the estimation of H_2ReCl_6 in the presence of HReO_4 , reference should be made to further work by Geilmann and Hurd,[†] the H_2ReCl_6 being precipitated separately as a salt of N,N' tetramethyl-*o*-tolidine.

A semi-quantitative colour test for rhenium may also be mentioned. I. and W. Noddack[‡] have shown that rhenium, as a perrhenate, gives a colour reaction on adding a thiocyanate. The reaction, in the course of which a complex rhenium thiocyanate is formed, is very sensitive. A yellow or red coloration is developed (slowly on boiling or rapidly if stannous chloride is added), the intensity of which can, by comparison with a solution of known rhenium content, be used to give an approximate indication of the amount of rhenium present. Geilmann, Wrigge, and Weibke[§] give the following details of suitable conditions for the test. Five cubic centimetres of the neutralized solution to be tested, 1–2 c.c. of 20 per cent. hydrochloric acid, 0.5 c.c. of 10 per cent. potassium thiocyanate, and several drops (at the most 0.5 c.c.) of a 10 per cent. solution of stannous chloride are mixed together. Small amounts of rhenium lead to a yellow colour. Larger quantities give a yellowish-red or red tint. The colour is soluble in ether.

[†] W. Geilmann and L. C. Hurd, *ibid.* 1933, **213**, 336.

[‡] I. and W. Noddack, *ibid.* 1929, **181**, 19.

[§] W. Geilmann, F. W. Wrigge, and F. Weibke, *ibid.* 1932, **208**, 217.

VI

SOME REACTIONS IN DISCHARGE TUBES

THE stream of electrons corresponding with the passage of an electrical discharge through a gas at a low pressure may be regarded as tantamount to the introduction of projectiles which, by collision with the gas molecules, raise these to high-energy states. Small particles such as electrons are not, unless specially accelerated to very high velocities, sufficiently energetic to cause nuclear reactions; but the energy acquired by a target molecule as the result of such collisions may be sufficient to rupture chemical bonds, and thus to cause dissociation, or to affect the electronic levels sufficiently to cause the ejection of electrons from the extranuclear structure, with the formation of positive ions which move in the opposite direction to the electron stream. These activation effects are in addition to any that may be caused photochemically by the adsorption of photons from the light which accompanies the discharge.

The so-called 'active species' produced by these collisions may revert to the ground state without chemical change; but, if the rupture of a chemical bond takes place, a free atom or a free radical may be produced which persists in a free state for a time dependent on the conditions. Alternatively, the active species may, while still in a high-energy or intermediate state, react with another molecule of the gas in such a way as to give a more complicated product. There is, moreover, in these discharge-tube processes, often evidence that the formation of secondary products is dependent on three-body collision processes.

The presence of the free atoms, free radicals, and other complexes can in many cases be detected spectroscopically. It should be noted, further, that, in addition to the discharge-tube method dealt with in the present chapter, many of these radicals may also be produced by irradiation processes, including resonance methods of the type described on p. 82 for active hydrogen.

PRODUCTION OF ATOMIC AND OTHER ACTIVE FORMS OF ELEMENTS

The formation of active hydrogen has already been considered. Many other gaseous elements yield short-lived free atoms on being passed at a low pressure through a discharge tube, the presence of

the element in the atomic state being deduced not only by its activity but also, in general, by the line spectra which are characteristic of free atoms, in contradistinction to the band spectra given by molecules.

Atomic Oxygen

While the principal long-life product of the action of a glow discharge on oxygen at atmospheric pressure is ozone, it has been shown by Wrede and others† that atomic oxygen, having a life of the order of that of atomic hydrogen, can be obtained in appreciable concentrations at low gas pressures. The formation of atomic oxygen in a discharge tube of the usual form was further studied by Harteck and Kopsch,‡ who employed an oxygen pressure of 1 mm. and a streaming-rate of about 3 metres per second.

Like atomic hydrogen, the free oxygen atoms recombine with evolution of heat on striking a suitable contact body. Thus, a thin platinum wire placed in the streaming gas quickly becomes incandescent; and it was found possible to use this rise in temperature, under standardized conditions, as a means of measuring the oxygen atom concentration. The heat of dissociation of oxygen is -117.3 Cals. With the discharge tube used by Harteck and Kopsch, the oxygen atom concentration in the gas stream was about 25–30 per cent. at a point 12 cm. from the discharge tube and probably of the order of 80 per cent. several centimetres from the discharge.

One of the most interesting reactions of atomic oxygen is its capacity to combine directly with diatomic oxygen with formation of ozone, which may readily be obtained by rapidly condensing the gas stream with liquid air. It seems probable, accordingly, that atomic oxygen is an intermediate product in ordinary ozone formation. Atomic oxygen does not react appreciably at room temperature with hydrogen or carbon monoxide; but it reacts energetically with methyl alcohol or with hydrocarbons such as benzene or acetylene, the process being accompanied by a glow or a flame. Methane, however, is not oxidized at room temperature. Carbon disulphide and hydrogen sulphide each react with a steel-blue intensive flame; and oxidation also occurs with hydrogen chloride or bromide. A frequently

† E. Wrede, *Z. Physik*, 1929, **54**, 53; Z. Bay and W. Steiner, *Z. physikal. Chem.* 1929, **B 3**, 149; C. Copeland, *Phys. Rev.* 1930, **36**, 1221.

‡ P. Harteck and U. Kopsch, *Z. physikal. Chem.* 1931, **B 12**, 327.

used test for atomic oxygen is its characteristic greenish-white luminescence with nitric oxide.

Recent Work on Active Nitrogen

As was shown by Strutt† in 1911, the action of a discharge on nitrogen at low pressures leads both to its chemical activation and to the production of a long-lived afterglow, the spectrum of which has a band structure and is thus apparently derived from molecular rather than from atomic nitrogen. The length of life of this afterglow (of the order of several hours under favourable conditions) points to the attainment, by the excited nitrogen molecules, of metastable levels from which the fall in energy giving the glow only occurs readily under rarely occurring conditions which probably involve some form of three-body collision (see later).

While detailed treatment of earlier work does not fall within the scope of the present section, it is convenient to summarize some of the fundamental data. The nitrogen is passed, usually under streaming conditions and at a pressure of, for instance, 0.5 mm., through a discharge tube provided with sealed-in metallic electrodes; or the excitation may be induced by an electrodeless discharge derived from an external winding. The streaming gas issuing from the discharge tube shows a characteristic yellow afterglow, the intensity of which is increased if the gas is cooled to liquid air temperature or, to a lesser degree, if it is compressed or mixed with unactivated nitrogen. The production of the glow is also stimulated by the presence in the nitrogen of traces of oxygen‡ or of certain other foreign gases; although Baker and Strutt§ have shown that activation can be obtained with pure nitrogen. The life of the afterglow, on storage of the activated gas in closed vessels depends on the nature of the containing surface: thus Rayleigh|| states that the glow was still visible after more than 5½ hours in a glass container coated internally with metaphosphoric acid.

In addition to showing this afterglow, the activated gas was found by Rayleigh to form nitrides with the vapours of various elements

† R. J. Strutt (Lord Rayleigh), *Proc. Roy. Soc.* 1911, A 85, 219; 1912, A 86, 56, 262; A 87, 179; 1913, A 88, 539.

‡ E. Tiede and E. Domecke, *Ber.* 1914, 47, 420.

§ H. B. Baker and R. J. Strutt, *ibid.* 1914, 47, 801, 1049; see also H. B. Baker, E. Tiede, R. J. Strutt, and E. Domecke, *ibid.* 1914, 47, 2283.

|| Rayleigh, *Proc. Roy. Soc.* 1935, A 151, 567.

(e.g. sodium, arsenic, or phosphorus) and to give, when mixed with iodine vapour, a bright blue luminescence, a coloured illustration of which is included in Rayleigh's first paper. In later work by Tiede and Knoblauch† the nitride obtained by shaking the active gas with mercury was analysed quantitatively and found to correspond with the normal formula, Hg_3N .

If active nitrogen is brought into contact with a suitable metallic target, catalytic stabilization of the nitrogen may take place without nitride formation, the target becoming heated by the stabilization energy. Copper and gold are especially effective; but many other metals‡ possess this property. A further effect, which was first described by Rayleigh and which has attained some importance as a method of detecting and measuring the concentration of the active modification, is its reaction with nitric oxide. This occurs with a white fluorescence and leads to nitrogen peroxide and inactive nitrogen.

It should be noted, firstly, that the chemical activity of the gas is either partly or completely independent of the molecular decay process which gives the glow and that, secondly, this glow process corresponds with only a very small fraction of the total decay energy. Thus, Willey§ has shown that the chemical activity (formation of nitrides, catalytic stabilization on metallic surfaces with rise in temperature, reaction with nitric oxide, etc.) may be observed even in the absence of the afterglow. In this work the glow in a stream of active nitrogen was destroyed by passage through a second and weaker discharge.|| The resulting non-luminous gas stream was then passed over a copper surface, which became heated by the catalytic stabilization of the active nitrogen. In other cases the non-luminous gas was mixed with nitric oxide, when the characteristic greenish-white flame and formation of nitrogen peroxide occurred.

The small contribution of the glow process towards the total decay mechanism has more recently been emphasized by Rayleigh,¶ who compared the total energy evolved during the catalytic stabilization of activated nitrogen at a gold surface with the energy emitted by reason of the glow. In a typical experiment the energy of stabilization per c.c., reduced to N.T.P., of total nitrogen treated was 4.5×10^8

† E. Tiede and H. G. Knoblauch, *Ber.* 1935, **68**, 1149.

‡ E. J. B. Willey, *J. Chem. Soc.* 1927, 2188.

§ E. J. B. Willey, *ibid.*, p. 2831.

|| Rayleigh, *Proc. Roy. Soc.* 1916, A **92**, 438.

¶ Rayleigh, *ibid.* 1940, A **176**, 16.

ergs (equivalent to about 10 eV per molecule of nitrogen), compared with 6.45×10^5 ergs due to the process giving the glow. This latter figure represented the energy value of the total light emitted during the whole of the period of the glow. Accordingly, the afterglow light represents a quite insignificant fraction (of the order of one-thousandth) of the total decay process. It would therefore seem that the considerable amount of work which has been done on the spectroscopy of the glow gives information on what is only a subsidiary part of the mechanism by which the energy of the activated nitrogen is lost.

Rayleigh† also used the integrated energy value of the light emitted as afterglow by a known volume of nitrogen under favourable conditions of excitation to calculate the fraction of the total molecules of nitrogen present which is evolved in the emission of the glow. On the basis of the emission, by each active nitrogen molecule, of one quantum of the mean size (corresponding with $\lambda = 5,560$) involved in the decay, it was estimated that, in a given test, a total of only 0.13 per cent. of all the molecules present had been active from the standpoint of emitting the afterglow.

In view of all the above facts, it is becoming increasingly evident that more work is required on the influence of various factors on the intensity and rate of decay of the chemical activity, as distinct from the glow, including the relationship between this activity and the concentration of any nitrogen atoms and the possible role played by atomic nitrogen in the chemical activity. In the meantime, a number of interesting further observations have been made on the mechanism of the influence of foreign gases on the intensity of the glow. This now appears to be a wall effect, due to adsorption and to consequent changes in the nature of the containing surface.

Influence of the Wall

In addition to the effect of foreign gases such as oxygen in intensifying the glow process, the afterglow in stored active nitrogen is known to be increased by adding unexcited nitrogen‡ or by compression. These factors, when considered in conjunction with the slowness of the decay, as shown by the long duration of the afterglow, all suggest some form of three-body collision process as the mechanism of the reaction giving the glow.

† Rayleigh, *Proc. Roy. Soc.* 1940, A 176, 1.

‡ H. O. Kneser, *Erg. exakt. Wiss.* 1929, 8, 229; Rayleigh, *Proc. Roy. Soc.* 1940, loc. cit.

It is known, further, that the state of the wall of the containing vessel plays what is often a dominant part in prolonging or shortening the life of the afterglow. The prolongation of the afterglow for several hours by coating the bulb with phosphoric acid has already been mentioned: the same effect is obtained with sulphuric acid. Herzberg† found that strong preliminary heating of glass *in vacuo* makes it destructive of the glow; and Rayleigh‡ has shown that preliminary heating in nitrogen also has this effect, whereas subsequent heating in oxygen, even at a pressure of 1 mm., restores to the glass its usual low activity towards the decay of the glow.

Rayleigh describes an interesting experiment which seems to show that the beneficial influence of small traces of oxygen in the production of active nitrogen under the usual conditions is a wall effect. In this experiment the activation of a stream of pure nitrogen, maintained at a pressure of 6 mm., was effected by a small condensed spark discharge in the centre of a 500 c.c. bulb. A small orange aureole, which gave the characteristic afterglow spectrum of active nitrogen, was formed around the spark and remained luminous for a second or so after discontinuing the discharge. The aureole did not reach as far as the walls of the bulb, at any rate not in any great strength. Addition of oxygen to the nitrogen under these conditions (limitation of the glow to a region away from the walls) decreased the afterglow, in place of increasing it as under normal conditions. It may also be noted that when a small tributary stream of oxygen is added to an ordinary discharge tube, a time lag occurs before the beneficial effect on the glow is observed: similarly, on discontinuing the oxygen, the foreign gas effect persists for a short time afterwards. These effects also can be interpreted to mean that the action of the oxygen or other impurity is to modify the wall by the formation of an adsorbed layer which requires a short time both for its formation and for its removal on re-passing pure nitrogen.

Mechanism of the Activation and Decay

The exact nature of the processes involved in the excitation and in the main part of the subsequent decay is still imperfectly understood, particularly since the molecular decay process giving the glow—on which the greater part of the experimental work has been

† G. Herzberg, *Z. Physik*, 1928, **46**, 878.

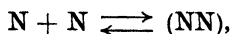
‡ Rayleigh, *Proc. Roy. Soc.* 1942, A **180**, 123.

done—appears, in view of Rayleigh's measurements, only to be responsible for the emission of a very small fraction of the total decay energy.

It seems certain that the excitation of the nitrogen by the discharge is accompanied by some dissociation. Thus Bay and Steiner† obtained spectroscopic evidence for the presence of nitrogen atoms in active nitrogen; but the statements in the literature as to the extent of this dissociation are contradictory. Crew and Hulbert‡ report that no measurable increase in pressure occurred on activation in a closed system at pressures between 0.08 and 0.55 mm. and infer that atomic nitrogen is not produced in large quantities. Debeau§ found, on the other hand, that if an electrodeless discharge was applied to a closed volume of low-pressure nitrogen, the pressure rose to almost twice its original value (about 0.5 mm.) for only a slight increase in the average temperature of the wall of the containing vessel.

On the basis of this indication of substantially complete dissociation as the first step, Debeau points out that if one-half of the atoms are in the metastable 2D state and the remainder in the normal 4S state, their fall to the ordinary ground state of molecular nitrogen would lead to the emission of 9.84 eV per molecule, which is about the value (10 eV) found by Rayleigh for the total decay energy.

Debeau postulates, as the first stage in the recombination, the formation of a collision complex (NN) by the process



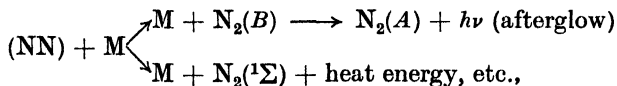
this being followed by alternative decay paths either by way of the glow process or by a path in which the energy is dissipated as heat or radiation not in the afterglow region or in the excitation of a collision partner, which is assumed to be necessary for reaction in each case. The afterglow is known from spectroscopic data to originate in the high vibrational levels in the $B^3\Pi$ state of molecular nitrogen and to lead to the production of metastable $A^3\Sigma$ molecules. Consequently, nitrogen in the B state must be one of the products of the recombination of the nitrogen atoms: further, the energy level of nitrogen molecules formed from atoms of the energies given above will be approximately that which is known to give rise to the glow.

† Z. Bay and W. Steiner, *Z. physikal. Chem.* 1929, B 3, 155.

‡ W. H. Crew and E. O. Hulbert, *Phys. Rev.* 1927, 30, 135.

§ D. E. Debeau, *ibid.* 1942, 61, 668.

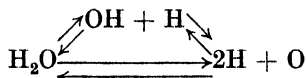
The alternative decay paths followed in the decay of the postulated collision complex can be written



in which M is the collision partner and $^1\Sigma$ is the ordinary ground state of molecular nitrogen. Debeau supports the above mechanism by evidence based on the effect of cooling part of the system to liquid air temperature, for details of which reference should be made to the original paper.

FREE HYDROXYL, OH

The hydroxyl radical is characterized spectroscopically, both in emission and in absorption, by a strong band at 3,064 Å, which has long been known to occur when substances containing hydrogen are burnt or in the spectra of electric discharges in gaseous or liquid water. The occurrence of this band in thermally dissociated water vapour has been studied by Bonhoeffer and Reichardt,[†] who state that, at high temperatures, the dissociation may take place to a greater extent by the hydroxyl route



than by the alternative direct production of hydrogen and oxygen.

In discharge tubes there appears to be no doubt[‡] that the principal primary reaction induced by electron impact on the water molecules is the production of hydroxyl and hydrogen. Of these, the hydroxyl radical is certainly in an excited state, as is shown by its emission spectrum; but no free oxygen atoms can be detected,[§] which would be the case if the electron-impact reaction proceeded appreciably by the alternative direct route. The absence of free oxygen atoms in the gases flowing from the discharge tube was also demonstrated, at any rate for moderate discharges, by Rodebush and Wahl^{||} and by Speakman and Rodebush[¶] by the absence of the characteristic greenish-white luminescence on bringing these gases into contact with nitric oxide.

[†] K. F. Bonhoeffer and H. Reichardt, *Z. physikal. Chem.* 1928, **139**, 75.

[‡] O. Oldenberg, *J. Chem. Phys.* 1935, **3**, 265.

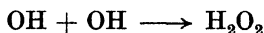
[§] G. I. Lavin and F. B. Stewart, *Proc. Nat. Acad. Sci.* 1929, **15**, 829.

^{||} W. H. Rodebush and M. H. Wahl, *J. Chem. Phys.* 1933, **1**, 696.

[¶] M. L. Speakman and W. H. Rodebush, *J. Amer. Chem. Soc.* 1935, **57**, 1474.

The formation of hydroxyl takes place equally readily in tubes provided with electrodes or in an electrodeless discharge. It is most pronounced at pressures of about 1 to 3 mm. Hydroxyl is a radical of moderately long life; and the course of its disappearance in a discharge tube after interrupting the discharge, or in a streaming gas, can be followed by observing the rate of fading of its absorption spectrum: thus Oldenberg,[†] working with a discharge tube at 1 mm. pressure, was able to trace the decay through a period of 0.4 sec. after cutting off the discharge.

If the streaming gas, after the discharge, is passed through a trap cooled with liquid air, considerable quantities of hydrogen peroxide are condensed;[‡] but the process



takes place in the cooled trap and no hydrogen peroxide can be detected either in the discharge tube§ or in a trap substantially above -100° . Accordingly no hydrogen peroxide is condensed in a trap immersed in melting ice.

The mode of disappearance of hydroxyl at higher temperatures, for instance in a discharge tube after discontinuing the discharge, has been studied by a number of workers, above all by Oldenberg and his collaborators.||

In Oldenberg's work the absorption band at 3,064 Å was highly dispersed by means of a 21-foot concave diffraction grating and the decay with time of the spectrum lines thus obtained was measured photographically in snapshots taken at intervals of 1/100th sec. These lines are sharp but faint under the conditions of high dispersion employed; and, in order to give a sufficient exposure to produce satisfactory photographs, it is necessary to repeat many times the series of snapshots. This was done automatically by a shutter synchronized to start the series with the interruption of the discharge.

From the observed kinetics, the disappearance of the hydroxyl was shown to be a far slower reaction than the very fast processes corresponding with the recombination of any ions present and to

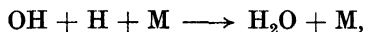
[†] O. Oldenberg, *J. Phys. Chem.* 1937, **41**, 293; *Phys. Rev.* 1934, **46**, 210.

[‡] Rodebush and Wahl, loc. cit.; K. H. Geib, *J. Chem. Phys.* 1936, **4**, 391; Lavin and Stewart, loc. cit.

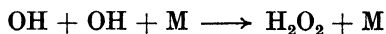
[§] R. W. Campbell and W. H. Rodebush, *J. Chem. Phys.* 1936, **4**, 293.

|| A. A. Frost and O. Oldenberg, *Phys. Rev.* 1935, **47**, 788; *J. Chem. Phys.* 1936, **4**, 642; A. A. Frost, D. W. Mann, and O. Oldenberg, *J. Opt. Soc. America*, 1937, **27**, 147.

involve almost certainly a three-body collision. Under favourable conditions, the fading of the hydroxyl lines could, as already stated, be followed for 0.4 sec. By far the greater part of the process takes place in the gas phase, by collisions involving water molecules, and only a slight wall reaction was obtained on clean glass walls. If, however, the interior of the discharge tube is covered with potassium chloride,† the reaction at the wall may be considerable. Oldenberg regards the most probable course of the homogeneous reaction to be



in which M is usually a water molecule; and this mechanism has also been accepted by other authors.‡ The alternative course



is regarded as being far less probable by reason of the absence of hydrogen peroxide in the discharge tube, although this is of course formed at liquid air temperatures. Evidence for this view is also provided by the work of Frost and Oldenberg,§ in which a stream of gaseous low-pressure hydrogen peroxide was used in the discharge tube, the rate of streaming being rapid in order to minimize the decomposition of the peroxide.

The chemical properties of hydroxyl are not very definitely known. Urey and Lavin|| mixed ethylene with the gases issuing from a water discharge tube and obtained a condensate which smelt of acetaldehyde, gave the iodoform test, and reduced Fehling's solution; and Jackson¶ observed oxidation reactions such as the conversion of carbon monoxide to the dioxide by the effluent gas. In view, however, of the possible presence of substances other than hydroxyl (even after the removal, as in Jackson's work, of any hydrogen or oxygen atoms by contact with platinum), further work seems to be necessary.

A closely related free radical, perhydroxyl, HO_2 , has been assumed as a first product of the association of hydrogen atoms and oxygen molecules;†† but Rodebush, Wende, and Campbell‡‡ consider that

† See also W. V. Smith, *J. Chem. Phys.* 1943, **11**, 110.

‡ For a summary, see T. G. Pearson, *Ann. Reports Chem. Soc.* 1937, **34**, 272.

§ A. A. Frost and O. Oldenberg, *J. Chem. Phys.* 1936, **4**, 781.

|| H. C. Urey and G. I. Lavin, *J. Amer. Chem. Soc.* 1929, **51**, 3290.

¶ W. F. Jackson, *ibid.* 1932, **54**, 1910.

†† K. F. Bonhoeffer and F. Haber, *Z. physikal. Chem.* 1928, A **137**, 263; W. Frankenburger and H. Klinkhardt, *Trans. Faraday Soc.* 1931, **27**, 431; J. R. Bates, *J. Chem. Phys.* 1936, **1**, 457.

‡‡ W. H. Rodebush, C. W. J. Wende, and R. W. Campbell, *J. Amer. Chem. Soc.* 1937, **59**, 1924.

there is no evidence for the formation of HO_2 in discharge tubes save as a 'collision complex' of very short life.

HIGHER OXIDES OF NITROGEN AND PHOSPHORUS

NO_3

The formation of an oxide of nitrogen higher than the pentoxide by the passage of a mixture of oxygen and nitrogen peroxide through a Siemens ozone tube was claimed as long ago as in 1881 by Hautefeuille and Chappuis,[†] mainly on grounds of the production of new absorption bands (at about 664 and 624 $\mu\mu$) due neither to ozone nor to ordinary oxides of nitrogen. Warburg and Leithäuser[‡] found that the production of the new oxide involved the action of ozone, formed in the reaction tube, on the lower oxides of nitrogen, since the same absorption spectrum was obtained, even in the absence of a discharge, if ozone was allowed to react with N_2O_5 . The correspondence of the oxide with the composition NO_3 or N_2O_6 follows principally from

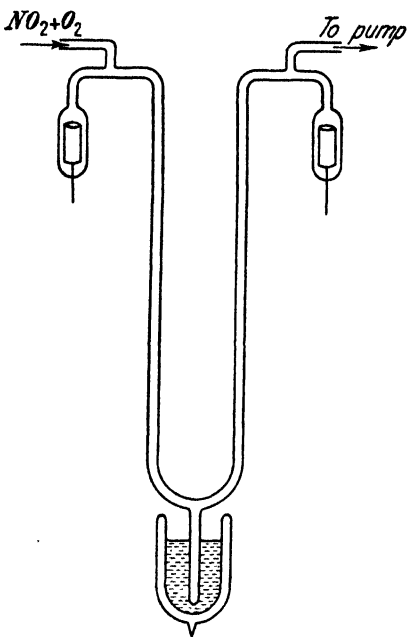


FIG. 23.

the work of Schumacher and Sprenger,[§] who also examined in considerable detail the mechanism and kinetics of its formation.

Schwarz and Achenbach^{||} examined the production of this oxide in a discharge tube of the form shown in Fig. 23. On passing a mixture of NO_2 and oxygen, for instance in the ratio of 1 to 20 and at a pressure of 1 mm., a white condensate was obtained in the liquid air trap. This condensate was analysed by allowing it to react with a known quantity of stannous chloride solution. From the quantity

[†] P. Hautefeuille and J. Chappuis, *Compt. rend.* 1881, **92**, 80; 1882, **94**, 1112, 1306.

[‡] E. Warburg and G. Leithäuser, *Ann. Physik*, 1906, **20**, 743; 1907, **23**, 209.

[§] H. J. Schumacher and G. Sprenger, *Z. physikal. Chem.* 1928, **A 136**, 77; 1929, **A 140**, 281; 1929, **B 2**, 267; *Z. angew. Chem.* 1929, **42**, 697; *Z. anorg. Chem.* 1937, **233**, 47.

^{||} R. Schwarz and H. Achenbach, *Ber.* 1935, **68**, 343.

of N_2O evolved and of stannous chloride oxidized (which was estimated by back titration with iodine), the ratio of N_2 to O was calculated. This was about 1 to 6 (the actual values in two experiments were 1 to 5.95 and 1 to 5.97), pointing to a composition N_2O_6 or NO_3 . The monomeric formula, NO_3 , appears probable both from the spectrum and from the difficulty in condensation; and Schwarz and Achenbach ascribe to it the formula $\text{O}:\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. These authors

state that the oxide is stable below about -140° and that it decomposes at higher temperatures to products which include NO_2 .

Apart from its condensation at the temperature of liquid air, the production of high concentrations of the oxide in the gas phase in a discharge tube or by the direct action of ozone is prevented by equilibrium conditions. Thus it has been estimated that the concentration of NO_3 in a gas mixture containing originally a partial pressure of 60 mm. of N_2O_5 and 60 mm. of ozone is less than 1 per cent. of the total nitrogen oxides present. Consequently, little is known of its chemical properties; and its presence has to be deduced solely from its spectrum.

It liberates iodine from iodides but does not give hydrogen peroxide on hydrolysis with water. It is thus apparently not identical with the oxide, $\text{NO}_2 \cdot \text{O} \cdot \text{O} \cdot \text{NO}_2$, prepared by Triponow† by the action of N_2O_5 on hydrogen peroxide.

It should be noted that the formation of NO_3 from NO_2 and oxygen in the glow discharge has been criticized by Klemenc and Neumann‡ on grounds that they were unable to freeze out a product which evolved oxygen on being removed from the liquid air bath. They report also that, under their experimental conditions, substantially the whole (95 per cent.) of the NO_2 was destroyed by the discharge. Klemenc and Neumann were, however, able to obtain NO_3 by evaporating a mixture of liquid ozone and NO_2 ; and they give a photograph of the characteristic absorption bands beginning, respectively, at 6,598 Å and between 6,217 and 6,266 Å.

P_2O_6 or PO_3

The somewhat similar production of this oxide of phosphorus has been observed by Schenk, Platz, and Rehaag.§ A mixture of

† I. Triponow, *Z. anorg. Chem.* 1922, **124**, 123.

‡ A. Klemenc and W. Neumann, *ibid.* 1937, **232**, 216.

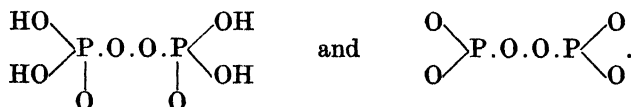
§ P. W. Schenk and H. Platz, *Naturwiss.* 1936, **24**, 651; P. W. Schenk and H. Rehaag, *Z. anorg. Chem.* 1937, **233**, 403.

phosphorus pentoxide vapour and oxygen was passed, at a pressure of about 1 mm., through a U-shaped discharge tube, part of which was cooled in ice, when a violet condensate was obtained in the cooled portion. This deposit showed evidence for the presence of a higher oxide by evolving oxygen on being heated to 130°.

The higher oxide could be separated to some extent from the P_2O_5 , which is also present in the deposit, by extracting this in a Soxhlet apparatus with dry chloroform, in which the P_2O_5 is preferentially soluble. In this way an enrichment up to about 11 per cent. of the higher oxide, calculated as P_2O_6 , was obtained, the concentration in the original deposit being about 6 per cent. The concentration of peroxide oxygen was estimated by the volume of this gas evolved on heating to 130°, also by titration of the iodine which is set free from potassium iodide.

Its probable composition follows from its reaction with water, the solution having properties identical with those of the perphosphoric acid prepared by the action of hydrogen peroxide on phosphoric acid. Thus the solution, in addition to liberating iodine from iodides, oxidized aniline to nitroso- and nitrobenzene and gave a purple coloration of permanganate on being added to a manganate. In aqueous solution, the phosphate could be removed by precipitation with magnesia mixture, leaving the higher acid in solution.

This oxide of phosphorus accordingly appears, unlike its nitrogen analogue, to be the anhydride of a per-acid; and Schenk considers the structural formula of this acid and of its anhydride, P_2O_6 , to be



NEW OXIDES OF SULPHUR

Sulphur Monoxide, SO

Henri and Wolff,† in 1929, called attention to a series of emission bands lying between 2,500 and 3,900 Å which occur in low-pressure discharge tubes containing sulphur dioxide. The bands in question differ from those ordinarily given by sulphur dioxide itself and were ascribed by these authors to sulphur monoxide, SO.

The isolation and the systematic examination of the properties of

† V. Henri and F. Wolff, *J. Phys. et Rad.* 1929, 10, 81.

this oxide are due principally to the work of Schenk and his co-workers,[†] who prepared it by the interaction of sulphur dioxide and sulphur vapour under streaming conditions at a low pressure and found that, if the effluent gas from the discharge tube is passed through a trap cooled in liquid air, an orange-red deposit, apparently consisting of polymeric sulphur monoxide, is obtained.

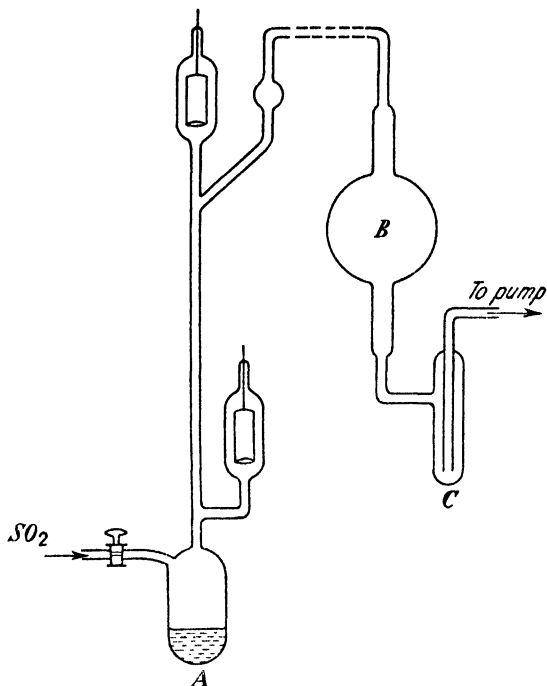


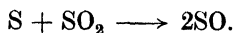
FIG. 24.

The essential parts of the apparatus used for the preparation of the purest product are shown diagrammatically in Fig. 24. The vertical discharge tube, *A*, which was about 1 m. in length and 20 mm. in diameter, was provided with aluminium electrodes and contained sulphur in its enlarged lower portion, which was heated to 250°. It was found unnecessary to heat the tube itself since this was maintained by the discharge at a temperature sufficient to prevent the condensation of sulphur on its walls. The stream of sulphur dioxide and sulphur, or of sulphur dioxide alone, was drawn at a low pressure

[†] P. W. Schenk, *Z. anorg. Chem.* 1933, **211**, 150; 1937, **233**, 385; H. Cordes and P. W. Schenk, *ibid.* 1933, **214**, 33.

through the apparatus by means of the pump, any sulphur emerging from the discharge tube being eliminated by condensation and by filtering off any dust. The gases, after being cooled in the large bulb, *B*, passed through the trap, *C*, which was cooled in liquid air.

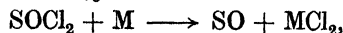
Although the reaction leading to the monoxide occurs to some extent with sulphur dioxide alone, far better yields were given if a mixture of sulphur vapour and sulphur dioxide was employed, the reaction being probably



Pure polymeric monoxide was obtained in the trap only if the sulphur was present in considerable excess. This excess of sulphur was condensed out separately prior to the intensive cooling of the gas stream. Since the emission spectrum can only be observed in the glow itself, the presence of the oxide beyond the discharge tube was followed by the absorption bands.

In the gaseous state, sulphur monoxide is probably dimeric;† and, although it readily undergoes further polymerization at low temperatures, this simple state may have a considerable life under suitable conditions, since the gaseous oxide can still be detected spectroscopically after several days of storage at room temperature in clean glass vessels, provided that these have previously been well baked out in a vacuum to remove adsorbed moisture. It is, however, stable only at low pressures. Thus, Cordes and Schenk were unable to compress the gas to a pressure higher than about 40 mm. without decomposition.

In addition to its formation in discharge tubes, sulphur monoxide may be made by the regulated combustion of sulphur in a 'cold' luminescent flame. This reaction‡ gives only small yields of the monoxide, with much dioxide, at atmospheric pressure; but, on decreasing the oxygen pressure to 5 mm., Schenk was able to obtain yields of sulphur monoxide up to 40 per cent. of the oxygen passed. Sulphur monoxide may, further, be made by the action of various metals on thionyl chloride,§



and it has been recognized spectroscopically as the primary product of the thermal decomposition of thionyl chloride or bromide.||

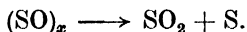
† E. Kondratieva and V. Kondratiev, *J. Phys. Chem. Russ.* 1940, **14**, 1528.

‡ P. W. Schenk, *Z. anorg. Chem.* 1934, **220**, 268; see also K. Heumann, *Ber.* 1883, **16**, 139.

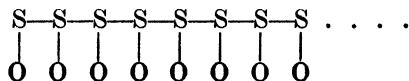
§ P. W. Schenk and H. Platz, *Z. anorg. Chem.* 1933, **215**, 113.

|| P. W. Schenk and H. Triebel, *ibid.* 1936, **229**, 305.

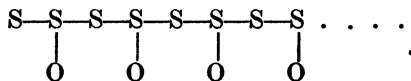
The empirical composition of the oxide follows with a reasonable degree of certainty from its formation from thionyl halides.[†] It has also been shown by Schenk[‡] that thionyl chloride may be made by injecting chlorine into the effluent gas produced by the discharge tube method. In the case of the orange-red polymer obtained by condensation at low temperatures, the ratio of sulphur to oxygen has been determined directly and found to be 1:1. The most conclusive evidence is to be found in Schenk's 1937 paper, since his earlier work assumes, for the decomposition of the orange polymer by heat, a simple quantitative course represented by



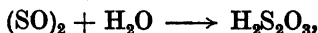
This decomposition was, in the course of later work, found to be more complicated, in that only a part of the oxygen contained in the polymer could be pumped off as sulphur dioxide on allowing the temperature to rise to that of the room. The evolution of gas then ceased completely; and the remaining oxygen was only liberated, as sulphur dioxide containing up to 50 per cent. of the monoxide, if the temperature of the polymer was very considerably increased: moreover, although the ratio between the easier and the more difficult stages of the decomposition varied somewhat, the average composition of the solid residue after the first stage was about S_2O , one-half of the oxygen contained in the original $(\text{SO})_x$ having been liberated in the first stage. Schenk suggests a primary polymer of the type



which passes, in the first stage of the decomposition, into



Little is known of the chemical properties either of the simpler gaseous (probably dimeric) monoxide, or of the more extensively polymerized substance, beyond the capacity of the former to add halogens with production of thionyl halides. It was claimed in an early paper[§] that, by interaction with water, sulphur monoxide gave thio-sulphuric acid according to the equation

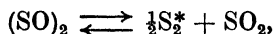


† E. Gruner, *ibid.* 1933, 212, 393; see also *Z. Elektrochem.* 1933, 39, 594.

† P. W. Schenk, *Z. anorg. Chem.* 1937, 233, 388.

§ Ibid. 1933, 211, 150.

from which the dimeric monoxide could be regarded as an anhydride of this acid; but later work appears to show that a mixture containing polythionic and other acids is produced. Neither the dimer nor the polymer reacts easily with molecular oxygen. The thermal decomposition of the dimer is simpler than that of the higher polymer and may correspond† with an equilibrium



in which the sulphur produced is in an excited state.

It should be noted, in connexion with the whole of the above work, that Cordes‡ has ascribed the series of absorption bands between 2,700 and 3,200 Å, which have been used for the spectroscopic identification of sulphur monoxide, to the presence of active sulphur rather than to any sulphur monoxide that may be present. This view has, however, been opposed by Schenk§ on grounds based on the non-production of the characteristic bands if oxygen is absent and on the various reactions involving the formation or decomposition of thionyl halides. Some of the differences in these opinions might be reconciled by considering any active sulphur present to be a decomposition product of the sulphur monoxide, as in Zeise's paper, since the bands appear whenever sulphur monoxide is formed, even at temperatures at which no appreciable quantity of elementary sulphur can be present as a gas; but Kondratieva and Kondratiev|| point out that the band spectrum in question is too complicated to be due to a diatomic molecule such as S_2 , although it is a probable structure for $(\text{SO})_2$; and it is evident that further work is required on the subject.

Sulphur Tetroxide, SO_4

Evidence pointing to the probable existence of a sulphur oxide higher than S_2O_7 has been obtained by a number of workers. Thus Meyer, Bailleul, and Henkel,¶ on passing a mixture of sulphur dioxide and oxygen through a Siemens ozonizer according to Berthelot's method†† of making S_2O_7 , obtained an oxide which was obviously a mixture but which approximated in the most favourable conditions

† H. Zeise, *Z. physikal. Chem.* 1942, B 51, 120.

‡ H. Cordes, *Z. Physik*, 1937, 105, 251.

§ P. W. Schenk, *ibid.* 1937, 106, 271; *Z. angew. Chem.* 1937, 50, 413; *Z. anorg. Chem.* 1937, 233, 385.

|| *Loc. cit.*

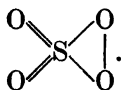
¶ F. Meyer, G. Bailleul, and G. Henkel, *Ber.* 1922, 55, 2923.

†† M. Berthelot, *Compt. rend.* 1878, 86, 277, 288.

to S_3O_{11} ; and Fichter and Maritz,[†] by the same method, were able to prepare an oxide mixture corresponding with a composition S_4O_{15} . A higher oxide of sulphur had also been made by Traube[‡] by the anodic oxidation of sulphuric acid. This oxide was not isolated; but, after removal of the sulphuric acid as the barium salt, was shown to have a ratio of SO_3 to O_{active} equal to 1:1.

The preparation of SO_4 in a pure state is due to Schwarz and Achenbach[§] who, on passing a mixture of dry oxygen and sulphur dioxide at a pressure of 0.5 mm. through a glow discharge tube of the usual form, were able to condense in a liquid air trap a solid white reaction product which could be purified to give substantially pure SO_4 . The best yields were obtained with an oxygen- SO_2 ratio of about 10:1, the oxygen being free from nitrogen to avoid the complication of nitrogen oxides. After the reaction the temperature of the condensate was allowed to rise to -30° ; and the product was freed from SO_2 and from any condensed or entrained ozone by passage of oxygen. The amount of the oxide produced was not large, about 0.1 g. being formed in 6 hours. It was analysed by precipitation as barium sulphate and iodometrically, and the ratio of SO_3 to active oxygen was shown to be approximately 1:1. Thus three specimens contained, respectively, 16.68, 16.40, and 16.66 per cent. of active oxygen, the theoretical percentage for SO_4 being 16.67.

Its molecular weight was determined cryoscopically in pure concentrated sulphuric acid, in which it dissolves without decomposition. Two determinations gave, respectively, values of 95 and 90, the theoretical value for SO_4 being 96. The oxide is accordingly monomeric. Schwarz and Achenbach ascribe to it the structural formula,



Sulphur tetroxide begins to decompose at about -5° , with evolution of oxygen. The decomposition pressure at this temperature is given as 0.5 mm. It melts at $+3^\circ$ (decomposition pressure 0.8 mm.) to an oily liquid which is apparently S_2O_7 . Solid SO_4 is stated to explode on being rubbed.

[†] F. Fichter and A. Maritz, *Helv. Chim. Acta*, 1939, **22**, 792.

[‡] M. Traube, *Ber.* 1889, **22**, 1518; 1891, **24**, 1764; 1892, **25**, 95; 1893, **26**, 1481.

[§] R. Schwarz and H. Achenbach, *Z. anorg. Chem.* 1934, **219**, 271.

In aqueous solution at low temperatures it seems to be fairly stable and not to undergo hydration to a per-acid; and the solution does not give the hydrogen peroxide reaction with titanyl sulphate or the blue coloration with acidified potassium dichromate. It also does not decolorize potassium permanganate; on the contrary, manganates are oxidized to permanganates. A solution of the tetroxide in benzene was found to oxidize aniline to nitroso- and nitrobenzene.

VII

THE PREPARATION AND USES OF ARTIFICIAL RADIOACTIVE ELEMENTS

THE recognition that bombardment may produce not only stable but also radioactive nuclei dates from 1934, in which year Curie and Joliot† prepared radioactive phosphorus, nitrogen, and silicon by the α -particle bombardment, respectively, of aluminium, beryllium, and magnesium.

Subsequent research has shown that the formation of this type of product is just as common as the alternative formation of ordinary stable nuclei: indeed, by 1940, as the result of intensive work by a large number of investigators, some three or four hundred artificial radio-elements had been prepared, covering the whole range of the periodic system from hydrogen up to the very heavy elements, which are in any case only known in a radioactive form, and including the hitherto not very definitely known element No. 85. The importance of this preparation of elements which, by virtue of their radioactive properties, can be used as tracers for indicating the path of individual atoms in chemical reactions and especially the occurrence of exchange, needs no stressing. The study of these radio-elements has also yielded new information with regard to nuclear energy states: thus the existence of so-called radio-isomers has indicated the presence of forbidden transitions between nuclear energy levels.

GENERAL

Since the general methods for the formation of unstable nuclei do not differ essentially from those involved in the formation of a stable nucleus (except for the special properties of the product), it will be convenient as an introduction first of all to deal in outline with some aspects which are common to both types of nuclear reaction. With this will be included a short summary of the principal points of similarity and difference between the properties of many of these artificial radio-elements and those of the naturally-occurring very heavy radioactive families contained in the radium, actinium, and thorium series, in which the atomic number approaches the limit for atomic existence even in a radioactive form.

† I. Curie and F. Joliot, *Compt. rend.* 1934, 198, 254.

The projectiles commonly used— α -particles, deuterons, protons, neutrons, and γ -ray photons—are the same for the production of both stable and unstable elements. In the case of charged particles, these are usually raised to a high velocity, and employed in the form of a highly concentrated stream, by the application of a cyclotron or other accelerating device; but particles which have a natural high energy of emission from a suitable radioactive source are also sometimes used: thus the α -particles used by Curie and Joliot in their discovery of artificial radioactivity were obtained directly from a polonium source and were used without acceleration. The intensity of the particle stream and the energies of the individual particles from a large cyclotron are very high. The 60-inch cyclotron employed by Lawrence and his co-workers at Berkeley is stated to be capable of producing deuteron currents up to 200 milliamperes with an energy of 16 Mev. Such deuterons are able to penetrate even into heavy nuclei, for which the potential barrier surrounding the nucleus is high. Even with currents of this intensity it was evident that there was a prospect of obtaining weighable amounts of artificial radioactive elements in a reasonable time. In the case of the heavier doubly charged α -particles, energies up to 32 Mev. are obtained from the same instrument, the current being, however, considerably less than with deuterons. All previous ideas of the magnitude of the possible preparation of artificial radio-elements have, of course, been revolutionized by the recent very large-scale war-time work on the production, principally by neutron bombardment, of artificial elements for atomic fission.

It may be noted that small particles such as electrons, even when raised to high velocities, are not, except at abnormally high accelerations, sufficiently energetic to cause nuclear disintegration; and small photons are also too low in energy to disintegrate a nucleus. Both X-ray photons and fast electrons have, however, been used for raising a nuclear energy-level through a range corresponding with the transformation of a stable atom into a radioactive nuclear isomer.

The use of neutrons as projectiles is of special interest since, owing to the absence of charge, these particles do not need to possess high energies to penetrate the nuclear potential barrier. Accordingly, slow neutrons may be added to a nucleus without adding sufficient energy to cause deeply seated disruption; and, in the type of work which has been developed especially by Fermi and his co-workers,

the velocity of neutrons employed for bombardment is, by passage through water or paraffin, artificially retarded down to a value at which the neutron is directly absorbed by the target nucleus. It will be seen that this process constitutes a simple method of forming an isotope the mass of which is one unit greater than that of the target element. These slow neutrons may have energies which are not greater than those which could be imparted thermally (e.g. of the order of one-fiftieth of an electron-volt). Neutrons of this low energy are accordingly sometimes called thermal neutrons. Neutrons of higher velocities are somewhat loosely described as medium, fast, and very fast, the last ranging up to 20 Mev.

In certain lower-energy ranges, interaction with a target nucleus occurs most easily if the neutron has one of a series of definite energy values, which vary with the nature of the target atom and correspond with nuclear resonance levels.

It may be noted that, since neutrons cannot be accelerated in any of the usual electrostatic devices, the upper limit of their velocity will depend on the nature of their source, including the energy of the projectiles used in their formation. Reference to some commonly used neutron sources has already been made on page 6. The nuclear reactions induced by fast neutrons are in many cases quite different from those induced by neutrons of low energy.

Nuclear Cross-sections

The chance of a reactive collision between a bombarding particle and a target nucleus is often expressed in terms of a conventionalized probability in which the cross-section of the particle is regarded as negligible.

It will be seen from Fig. 25 that if a surface, for instance, 1 cm. square, is occupied by N atoms (shown as larger circles) each containing a nucleus of cross-sectional area a , the probability of a direct hit on a nucleus by an impinging particle of negligible radius will be given by the ratio of the sum of the areas of the nuclear cross-sections to the residual area, namely, by $Na/(1-Na)$. Since the diameter of an atomic nucleus ($\sim 10^{-12}$ cm.) is very small in comparison with the order of magnitude of the diameter of the whole atom ($\sim 10^{-8}$ cm.), this probability reduces to Na or to $N\pi r^2$, in which r is the nuclear radius. Very similar considerations also apply if the bombarding projectile penetrates the surface to some extent, since the

probability that an individual nucleus in the target will directly screen a further nucleus is very small on account of the very small nuclear size.

Accordingly, if unit area of a target is bombarded with a stream of projectiles at a known rate, it would be expected that the number

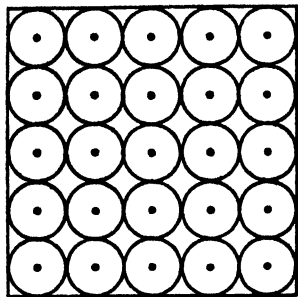


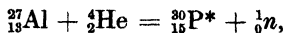
FIG. 25.

of collisions with nuclei could be calculated in the above manner, using the normal value, i.e. $\frac{1}{4}\pi(10^{-12})^2$ or about 10^{-24} cm.², for the nuclear cross-section. Actually, the observed stopping power is usually much greater than the calculated figure. Thus it is apparently not necessary to obtain a direct hit on a nucleus in the ordinary sense but merely for the projectile to come within a certain range which is greater than the ordinary nuclear radius;

or, expressed somewhat differently, the effective cross-section of a nucleus for a given bombardment reaction is usually far greater than its ordinary cross-section. Effective cross-sections up to 10^{-21} cm.² are known, such a figure being a thousand times the expected value.

Types of Nuclear Reactions

To shorten the writing of nuclear equations it has become conventional to employ a nomenclature in which the target element, the projectile, the emitted particle or radiation, and the new nucleus formed by the reaction are written in order. Thus, Curie and Joliot's original production of radiophosphorus,



is written ${}_{13}^{27}\text{Al}(\alpha, n){}_{15}^{30}\text{P}$ and is classed as an α, n reaction. The possession of radioactivity is often denoted by an asterisk.

The principal types of nuclear reactions are summarized in Table 74, the examples being in most cases taken from reactions involving the simpler radio-elements. For a discussion of the prevalence and ease of occurrence of the various reaction types as the atomic number scale is ascended, including the general effect of the energy of the projectiles on the type of reaction which is induced, reference may be made, for instance, to the review by Seaborg.[†] The table includes

[†] G. T. Seaborg, *Chem. Rev.* 1940, **27**, 199. This review has frequently been consulted in connexion with the preparation of the present chapter; and the author wishes to express his indebtedness for a number of the data given.

the relationship, for the reaction type in question, between the atomic and mass numbers of the product element and those of the target: thus a figure of, for instance, +1 in the third or fourth column of the table indicates that Z (or A) is raised by one unit.

TABLE 74

<i>Projectile</i>	<i>Reaction type</i>	<i>Effect on Z</i>	<i>Effect on A</i>	<i>Examples</i>
Neutrons . .	n, γ	0	+1	$^{23}_{11}\text{Na}(n, \gamma)^{24}_{11}\text{Na}^*$
	n, p	-1	0	$^{23}_{11}\text{Na}(n, p)^{23}_{10}\text{Ne}^*$
	n, α	-2	-3	$^{27}_{13}\text{Al}(n, \alpha)^{24}_{11}\text{Na}^*$
	$n, 2n$	0	-1	$^{35}_{17}\text{Cl}(n, 2n)^{34}_{17}\text{Cl}^*$
Protons . .	p, n	+1	0	$^{11}_5\text{B}(p, n)^{11}_6\text{C}^*$
	p, γ	+1	+1	$^{12}_6\text{C}(p, \gamma)^{13}_7\text{N}^*$
Deuterons . .	d, p	0	+1	$^{63}_{29}\text{Cu}(d, p)^{64}_{29}\text{Cu}^*$
	d, n	+1	+1	$^{12}_6\text{C}(d, n)^{13}_7\text{N}^*$
	d, α	-1	-2	$^{20}_{10}\text{Ne}(d, \alpha)^{18}_8\text{O}^*$
α -Particles . .	α, p	+1	+3	$^{40}_{20}\text{Ca}(\alpha, p)^{43}_{21}\text{Sc}^*$
	α, n	+2	+3	$^{12}_6\text{C}(\alpha, n)^{15}_8\text{O}^*$
γ -Rays . .	γ, n	0	-1	$^{16}_8\text{O}(\gamma, n)^{15}_8\text{O}^*$

In addition to nuclear reactions leading to a single atom the atomic weight of which is not greatly different from that of the target, the bombardment of heavy nuclei (uranium, protoactinium, or thorium) may lead to a nuclear cleavage† in which, usually, two radioactive fission fragments of intermediate size are formed. Fission is dealt with separately in a later chapter.

Much of the above general treatment applies both to nuclear reactions giving stable products as well as to those in which a radioactive nucleus is formed. In the remainder of the section the special properties which characterize unstable nuclei, namely their passage into a more stable form, will be considered. Although, in natural radioactivity, these processes are grouped under the heading of radioactive decay in the sense that the unstable nucleus ejects a part of its mass, a loss of mass does not occur in all cases in the wider range of processes involved with artificial radio-elements, e.g. in simple K -electron capture with emission of a γ -ray, or in the stabilization of a radio-isomer, unless these processes are viewed as involving a mass loss equivalent to the mass of the γ -ray photon emitted.

† O. Hahn and F. Strassmann, *Naturwiss.* 1939, 27, 11, 89.

Radioactive Stabilization Processes

It should be noted that the observed products of radioactive change are not necessarily directly emitted from the nucleus; and it is therefore necessary to differentiate clearly between primary or nuclear processes and secondary effects produced by the passage of nuclear particles or radiation through the extranuclear electronic structure.

The primary processes by means of which an unstable nucleus may become stabilized are more numerous for artificial radio-elements than for the heavy natural elements. Five types of nuclear change which have been well established are summarized in Table 75. The numbers in the second and third columns give the change in the atomic and mass numbers.

TABLE 75

<i>Nuclear process</i>	<i>Effect on Z</i>	<i>Effect on A</i>
α -Particle emission . .	-2	-4
Electron emission . .	+1	0
Positron emission . .	-1	0
K-electron capture . .	-1	0
γ -Ray emission . .	0	0

Disintegration by emission of an α -particle, which is common in the heavy natural series, is rare with lighter nuclei, but an example of α -activity is given by ${}^8\text{Li}^*$. The ejection of positrons is peculiar to artificial elements; and, since this particle is unstable and undergoes annihilation—with production of energy—by interaction with an electron, its emission is always accompanied by annihilation energy in the form of γ -rays (two quanta from each positron-electron reaction) of energy 0.51 Mev., corresponding with $m_e c^2$. K-electron capture is a general term for the capture of an extranuclear electron by an unstable nucleus; but, since K-electrons are nearest to the nucleus, it is from this shell that such a capture usually takes place. The capture leaves, in the extranuclear electronic structure, a gap which is filled by an electronic rearrangement, this rearrangement being accompanied by the emission of the radiation (X-rays) characteristic of such a change in electronic levels in the product element.

The emission of electrons (β -particles) has many points of interest. In the first place, these particles may be emitted directly from the

nucleus. Such electrons are characterized by an energy continuum (i.e. a continuous variation in energy) which, as already mentioned, forms the basis for the postulation of the existence of the neutrino. In addition, in the course of the passage of nuclear γ -rays from the nucleus outwards through the extranuclear structure, the energy of some of these photons may be absorbed by extranuclear electrons in the various shells, the energy of the absorbing electron being raised to a level sufficiently high for the ejection of the electron out of the atomic field. Such electrons are known as secondary or internal conversion electrons; and, since the initial or binding energy of electrons in the various shells differs by definite quantum steps, secondary electrons will have an energy 'line-structure' depending on the particular shell from which they have been ejected, the energy of a given electron being the difference between that of the γ -ray photon and the binding energy of the electron. Any secondary electrons ejected will, of course, leave an electronic gap which will be filled by rearrangement of the remaining electrons, the process being, as before, accompanied by the characteristic X-rays.

The final type of stabilization process given in the table, namely, the emission of γ -radiation, occurs as a single primary process in isomeric transition. It is also a common accompaniment of internal readjustment processes following the ejection of particles. Reference has already been made to the internal conversion of nuclear γ -rays.

The mathematical course of any stabilization process is, as would be expected, the same for artificial as for the natural radio-elements and accordingly requires little comment. In each case, since the rate is proportional to the number of unstable atoms,

$$N = N_0 e^{-\lambda t},$$

in which N_0 is the number of radioactive atoms at the time taken as zero, N is the number at time t , and λ is the decay constant. This decay constant has the dimensions of reciprocal time. It can be shown that the mean life of all the atoms present at zero time is $1/\lambda$. This is the so-called statistical life, τ . The half-lifetime, $t_{\frac{1}{2}}$, which is the time required for the reduction of the original number of radioactive atoms to one-half (or for the reduction of the original activity to one-half), is given by

$$t_{\frac{1}{2}} = (1/\lambda) \log_e 2 = 0.693/\lambda,$$

the relationship between τ and $t_{\frac{1}{2}}$ being thus: $t_{\frac{1}{2}} = 0.693 \tau$.

Since the decay of artificial radio-elements usually leads directly to stable nuclei in one stage, the complication of a large number of successive processes, which is characteristic of the long natural radioactive series, does not normally arise. Longer radioactive chains do, however, occur with fission products (see Chapter VIII).

Nuclear Isomerism

If a nucleus is raised, by impact or other means, to a high energy-level, it will in most cases (if the level is not sufficiently high to cause disintegration) revert to a more stable lower level at a velocity too great to be measured, the process being accompanied by the emission of radiation. Evidence has, however, accumulated which tends to show that this process may, in certain cases, be delayed by the existence of forbidden transitions (probably between rotational levels) for which the probability of occurrence is low. The stabilization process will accordingly come to a halt at these metastable states, the release from which will, according to the probability laws, take place at a definite rate which, if slow enough to be measured, will, in a given specimen of a metastable product, lead to an observable decay in the intensity of the γ -ray emission, which will vary exponentially with the time as the number of nuclei in the metastable state decreases.

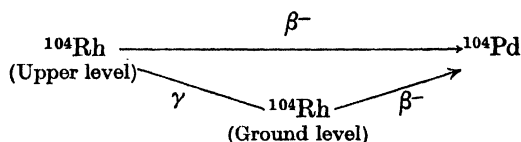
The whole process is thus strongly reminiscent of the control which underlies the whole phenomenon of radioactivity, in which, in place of the normal practically instantaneous regrouping or disintegration of an unstable nuclear system, the disintegration or other rearrangement is controlled by low-probability transitions (or by the 'leakage' of a particle-wave *through* a potential barrier).

Nuclear isomerism may involve transitions either to a lower but still unstable state or to a stable ground level: thus a nuclear isomer may be isomeric either with a further radioactive entity or with a stable element. A well-known example of the first of these types is given by the two radioactive isomers of $^{80}_{35}\text{Br}^*$, which exists in a higher-energy form, having a half-life of 4.4 hours, and emitting partly internally converted γ -rays, and in a lower-energy form of half-life 18 minutes, emitting nuclear β -particles and γ -radiation. The two forms of $^{44}_{20}\text{Sc}^*$, of half-life 52 and 4 hours, are a similar radioactive pair. Instances of the isomerism of a radioactive nucleus with a stable nucleus are found in $^{83}_{36}\text{Kr}$ and $^{87}_{38}\text{Sr}$, both of which exist either

in the form of a radioactive or a stable atom. It will be noted that these radioisomers have, in each case, identical mass and atomic numbers, the main observable differences lying in their radioactive properties.

Branched-Chain Stabilization

If, in any nucleus, there is a substantial probability of the independent occurrence of more than one type of stabilization process, each of these processes will take place in the proportion of its probability and the result will be a branching or alternative decay course. Branching is not very common with artificial radio-elements. As an example, the passage of the higher-energy radioisomer of ^{104}Rh to ^{104}Pd either directly or by a two-stage process of the nature



has been observed by Pontecorvo.†

Chemical Identification of Products of Nuclear Reactions

In order to identify a nucleus or an atom completely it is necessary to know both the atomic number, Z , and the mass number, A . The value of Z gives its identity as an element: the value of A states which isotope of the particular element is present.

The evaluation of Z usually resolves itself into a determination of the element with which the product under examination is isotopic and particularly of the element with which the product is always co-precipitated. Evidence on this point is obtained, in the case of radioactive products, by the transfer of the characteristic radioactivity to the precipitate and its disappearance from the solution. The use of isotopic carriers, which is usually a necessary procedure where the available amount of a product is too small to allow its direct examination, has already been worked out in detail for the chemical identification of members of the natural radioactive series and accordingly requires little discussion, since the standard methods are directly applicable throughout the whole range of artificial radio-

† B. Pontecorvo, *Phys. Rev.* 1938, **54**, 542; see also P. B. Moon, *Ann. Reports Chem. Soc.* 1938, **35**, 33.

elements. In most cases the probable nature of the product element can be predicted, or at least reduced to a small number of possibilities by considerations based on the target, the projectile, and any resultant particle, the number of probable carriers for trial being similarly reduced.

In addition to this carrier method, other means of separating a product element from a target can sometimes be employed if the properties of these are sufficiently different: thus a radioactive gas or a volatile element formed from a non-volatile target may be pumped off or removed in a gas stream, or an element such as radio-sodium may be separated by virtue of the solubility of its compounds. This solubility method was used by Segrè, Mackenzie, and Corson† for the separation of radiosodium produced by the bombardment of a magnesium target by fast electrons.

A special case of great interest in artificial radioactivity occurs if the product element is isotopic with the target, since both product and target will then have the same chemical properties and can no longer be separated by ordinary chemical means. The most important nuclear reactions leading to products of this nature are of the n, γ type, in which bombardment with a slow neutron leads to the inclusion of the neutron in the target nucleus with formation of an isotope in which the original mass number is increased by unity. Szilard and Chalmers‡ have shown that, in such cases, a target atom, originally present in a combined form, is, after this capture of a neutron, largely found in the free state and may thus be separated from the unaffected combined atoms in the target. In Szilard and Chalmers's original work, ethyl iodide was radiated with neutrons from a radium-beryllium source in order to produce radioiodine. On adding a trace of ordinary inactive iodine, extracting with water, and converting the whole of the soluble iodine to silver iodide, it was found that the activity of the precipitate was about ten times that of the residual ethyl iodide.

The primary cause of the separation of a radio-element by the Szilard and Chalmers method is the recoil of the radioactive nucleus following the emission of the γ -ray photon resulting from the capture of the neutron. It can be shown§ that, if E_γ is the energy of the

† E. Segrè, K. R. Mackenzie, and D. R. Corson, *Phys. Rev.* 1940, **57**, 1087.

‡ L. Szilard and T. A. Chalmers, *Nature*, 1934, **134**, 462.

§ C. S. Lu and S. Sugden, *J. Chem. Soc.* 1930, 1273.

γ -ray in electron-volts, m the mass of the atom ($H = 1$), and E_a the energy of the recoil in e.v., then

$$E_a = 5.33 \times 10^{-10} E_\gamma^2 / m.$$

This recoil energy is always much larger than the energy of rupture of a chemical bond: accordingly every halogen atom which captures a neutron will be liberated from its parent molecule and can react as a free radical.

The applicability of the method is very wide. Thus, in addition to the separation and concentration of radioactive halogens from bromoform, chloroform, and carbon tetrachloride, Amaldi and his co-workers† were able to separate a 35-minute radiochlorine, which had been liberated from sodium chlorate by neutron bombardment, by adding a trace of a chloride ion as a carrier followed by silver nitrate and dilute nitric acid to precipitate the total chloride while the chlorate remained in solution. Bromates and iodates behaved similarly, from 70 to 90 per cent. of the total radioactivity being concentrated in the precipitated silver halide. Other elements can be concentrated by appropriate precipitation: for instance, radioarsenic, from irradiated cacodylic acid, $(\text{CH}_3)_2\text{AsOOH}$, was precipitated as the sulphide. Further, on irradiating with slow neutrons a solution of potassium permanganate, the MnO_4^- ion was dissociated in such a way that the manganese was left in lower states of oxidation and, after the addition of a further small quantity of a manganous salt, could be co-precipitated with the carrier as the carbonate. The effectiveness of concentration by modifications of the Szilard and Chalmers method may be affected by exchange reactions with the parent molecule or with surrounding molecules during the extraction process.‡

It is to be noted that the liberated radio-elements can, especially in gaseous systems, be collected on a charged plate; but the charge is not necessarily inherent in the liberation process and is apparently often due to the attachment of the active element to free gaseous ions (both positive and negative), since this concentration occurs on electrodes of either sign. Radioiodine from irradiated gaseous methyl or ethyl iodide has been concentrated by Amaldi in this way, but

† E. Amaldi, O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segrè, *Proc. Roy. Soc.* 1935, A 149, 522.

‡ See O. D'Agostino, *Gazz.* 1935, 65, 1071; E. Glückauf and J. W. J. Fay, *J. Chem. Soc.* 1936, 390; W. F. Libby, *J. Amer. Chem. Soc.* 1940, 62, 1930.

the yield was rather poor. Fay and Paneth† used a similar method for concentrating the radioactive arsenic isotope, $^{76}\text{As}^*$, from gaseous arsine which had previously been irradiated with slow neutrons.

All the above remarks refer only to the determination of the chemical nature of a radioactive product, i.e. to the determination of Z . The assignment of the correct mass number, A —which is a necessary accompaniment for completing the identification of the isotope—cannot in most cases be carried out directly by means of a mass spectroscope on account of the small quantity of the product. Accordingly, A has to be obtained from the nuclear equation which can be derived from a knowledge of the entities (atoms, particles, and radiation) involved. This value of A is usually checked by the preparation of the same isotope, having identical chemical and radioactive properties, by alternative routes.

CONSIDERATION OF INDIVIDUAL RADIO-ELEMENTS

The preparation and properties of the simplest radio-element, $^3\text{H}^*$, have already been discussed in Chapter II. It is obviously impossible, for reasons of space, to deal in the present section with each radio-element individually; but the degree to which the discovery of artificial radioactivity has increased the number of isotopes now known can be judged from Table 76, which gives the isotopes, both stable and unstable of elements of atomic numbers 0 to 10. Radioactive isotopes are indicated by an asterisk. The symbol β^- stands for nuclear electrons as distinguished from internal-conversion electrons. K indicates K -electron capture. For a list including isotopes of heavier elements reference may be made, for instance, to the summary by Seaborg‡ (in which the complete list of radioactive isotopes alone occupies twenty-five closely printed pages).

In the remainder of the section some details of the preparation and chemical recognition of a few typical radio-elements will be given in order to illustrate the experimental methods used. Three points may be noted in this connexion:

- (i) Even if the target element is isotopically simple, alternative reaction routes (with a given projectile under given conditions) may be followed, leading to alternative products. Strictly, there is always a definite probability for concurrent processes;

† J. W. J. Fay and F. A. Paneth, *J. Chem. Soc.* 1936, 384.

‡ G. T. Seaborg, loc. cit.

TABLE 76

<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Half-life</i>	<i>Particles or radiation emitted (or type of decay)</i>
Neutron . . .	0	1	Stable	—
Hydrogen . . .	1	1	Stable	—
		2	Stable	—
		3*	31 years	β^-
Helium . . .	2	3	Stable	—
		4	Stable	—
		6*	0.8 sec.	β^-
Lithium . . .	3	6	Stable	—
		7	Stable	—
		8*	0.88 sec.	α, β^-
Beryllium . . .	4	7*	53 days	K, γ
		8	Stable	—
		9	Stable	—
		10*	$> 10^3$ years	β^-, γ
Boron . . .	5	10	Stable	—
		11	Stable	—
		12*	0.02 sec.	β^-
		10*	8.8 sec.	β^+
Carbon . . .	6	11*	21 min.	β^+
		12	Stable	—
		13	Stable	—
		14*	$> 10^3$ years	β^-
		13*	9.9 min.	β^+, γ
Nitrogen . . .	7	14	Stable	—
		15	Stable	—
		16*	8 sec.	β^-
		15	2 m. 6 sec.	β^+
		16	Stable	—
Oxygen . . .	8	17	Stable	—
		18	Stable	—
		19	31 sec.	β^-
		17*	1 m. 10 sec.	β^+
		18*	1 m. 52 sec.	β^+
Fluorine . . .	9	19	Stable	—
		20*	12 sec.	β^-, γ
		19*	20.3 sec.	β^+
		20	Stable	—
		21	Stable	—
Neon . . .	10	22	Stable	—
		23*	40 sec.	β^-

but if, as frequently occurs in practice, the probabilities for all save one main reaction are low, the product will be substantially single. This is, of course, analogous to straight-chain and branching decay in ordinary radioactive disintegration: however, unlike these spontaneous nuclear processes, the relative probability of alternative routes in nuclear reactions induced by bombardment can often be changed by changing the energy of the projectile (e.g. reactions with fast and slow neutrons).

- (ii) Similar probability laws will operate if the target element contains more than one isotope, with the additional complication of different products from the different isotopes. Again, however, there is often a main product or at any rate a main radioactive product, so that the observed activity is due substantially completely to a single atomic species. The preferential reaction of a given isotope does not appear to depend entirely on its abundance in the target (cf. the formation of the long-lived radiocarbon, ^{14}C , from the less abundant stable isotope, ^{13}C).
- (iii) A given radio-element can usually be made in a number of different ways. As has already been mentioned, considerations based on this production of a radio-element by cross reactions play an important part in fixing its mass number.

For reasons of space a large number of examples cannot be given. Accordingly, although radioactive isotopes are known over the whole range of the periodic system, any detailed treatment will be confined to five typical elements: sodium, carbon, sulphur, phosphorus, and bromine.

Preparation of Radiosodium

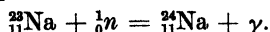
Natural sodium consists of a single stable isotope, ^{23}Na . The best-known unstable isotopes are ^{22}Na and ^{24}Na ; but the existence of a shortlived (23 sec.) isotope, ^{21}Na , has also been reported.

$^{24}\text{Na}^*$

In the work of Fermi and his collaborators,† neutrons derived from a radon-beryllium source were reduced to a low velocity by passage through paraffin and allowed to impinge on pure sodium carbonate. The activity of the irradiated substance could be resolved into two

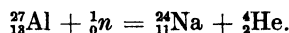
† E. Amaldi *et al.*, *Proc. Roy. Soc.* 1935, A 149, 522.

main activities, having half-lives respectively of about 40 seconds and 15 hours, the latter being due to ^{24}Na formed by the simple neutron-capture (n, γ) process



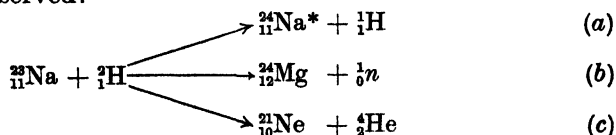
Its identity as sodium and the absence of active elements adjacent to sodium ($Z = 11$), namely, ${}_9\text{F}$, ${}_{10}\text{Ne}$, ${}_{12}\text{Mg}$, and ${}_{13}\text{Al}$, all of which are possible products, were shown by dissolving the irradiated salt in water, adding a little aluminium chloride and magnesium chloride as possible carriers, and precipitating these as hydroxides by adding ammonia. This precipitate was found to be inactive. To the radioactive solution, containing the sodium, a little sodium fluoride was added and the fluorine precipitated as barium fluoride which was inactive. The solution was evaporated to dryness and the residue ignited gently in case an isotope of neon had been formed and, by virtue of its small amount, was present in a dissolved state. The characteristic activity ($t_{\frac{1}{2}} = 15$ hrs., with emission of β -particles and γ -rays) remained in the dry sodium salt.

^{24}Na was also made by irradiating aluminium with faster neutrons. In this case an n, α reaction occurred:



The chemical identification was carried out in much the same way as that already described. The irradiated aluminium was dissolved in hydrochloric acid, small quantities of sodium and magnesium salts were added, and the aluminium and magnesium precipitated as hydroxide and phosphate, both of which were inactive. The solution containing the sodium was then evaporated to dryness. The dried residue showed the characteristic 15-hour β -activity.

A further method making ^{24}Na involves the process $^{23}\text{Na}(d, p)^{24}\text{Na}$. Lawrence† employed for the preparation a beam of 1.7 Mev. deuterons from a cyclotron. On irradiating sodium, as NaCl , three reactions were observed:



Reactions (a) and (b) took place to approximately the same extent and (c) to a subsidiary degree; but reaction (a) alone leads to a

† E. O. Lawrence, *Phys. Rev.* 1935, **47**, 17.

radioactive product, since ^{24}Mg , ^{21}Ne , and ^4He are stable isotopes. In Lawrence's experiments the rate of production of $^{24}\text{Na}^*$ was estimated at 4×10^6 atoms of radiosodium per microampere of 1.7 Mev. deuterons per second. ^{24}Na was identified as sodium by chemical tests as before.

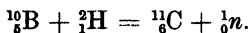
^{24}Na disintegrates by the emission of an equal number of β -particles and γ -ray photons, passing into ^{24}Mg . Later determinations of its half-life gave the value 14.8 hours.

Preparation of Radiocarbon

Carbon has two stable isotopes, ^{12}C and ^{13}C , having abundances respectively of 98.9 and 1.1 per cent. in the natural element. Its unstable isotopes are $^{10}\text{C}^*$ ($t_{\frac{1}{2}} = 8.8$ sec.), $^{11}\text{C}^*$ (21 min.), and $^{14}\text{C}^*$ ($> 10^3$ years). Of these, $^{11}\text{C}^*$ is best known; but the long-lived isotope, $^{14}\text{C}^*$, is of great interest from the standpoint of the convenience of its use in organic chemistry, since the lifetime of ^{11}C is too short for its employment in ordinary operations.

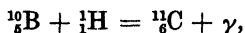
$^{11}\text{C}^*$

Yost, Ridenour, and Shinohara† made ^{11}C by the bombardment of boron (as fused boric oxide) with a 40-microampere beam of 0.9 Mev. deuterons, the reaction being



After irradiation, the target was heated to 600° in a current of air, when the activity passed into the gas stream. That the activity was due to carbon (partly as the dioxide and partly as the monoxide) was shown by completing the oxidation by passage, together with additional carbon monoxide as a carrier, over hot copper oxide. The activity could then be completely removed by absorption with potash. Its identity was further confirmed by the usual series of tests designed to eliminate adjacent elements.

^{11}C , having the characteristic half-life of 21 minutes, has also been made from boron by bombardment with protons,‡



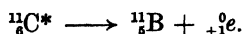
as well as by many other reactions (e.g. $^{11}\text{B}(p, n)^{11}\text{C}$, $^{12}\text{C}(n, 2n)^{11}\text{C}$, and $^{14}\text{N}(p, \alpha)^{11}\text{C}$).§

† D. M. Yost, L. N. Ridenour, and K. Shinohara, *J. Chem. Phys.* 1935, **3**, 133.

‡ H. R. Crane and C. C. Lauritsen, *Phys. Rev.* 1934, **45**, 497.

§ W. H. Barkas, *ibid.* 1939, **56**, 287; M. L. Pool, J. M. Cork, and R. L. Thornton, *ibid.* 1937, **52**, 239.

It disintegrates by positron emission to stable ^{11}B :



$^{14}\text{C}^*$

The first definite production of ^{14}C is due to Ruben and Kamen,[†] who bombarded a graphite target with a 40-microampere beam of 7–8 Mev. deuterons. After irradiation for 120 hours, the target was burnt in a stream of oxygen. The gas, after passage over heated copper oxide, was collected in a liquid air trap and subsequently absorbed by lime water, the precipitated CaCO_3 being washed and dried.

It was found that the precipitate contained the activity, which consisted of soft but detectable β -particle emission having a maximum energy of 0.09 ± 0.015 Mev. Since this is close to the known value for $^{35}\text{S}^*$, the possibility of the gas being $^{35}\text{S}^*\text{O}_2$ was eliminated by oxidation under conditions such that any sulphur would be oxidized to sulphate. To this end, the active gas was first absorbed in lime water, as above, then NaHSO_3 was added as a carrier, followed by permanganate in sulphuric acid solution. The carbon dioxide evolved still carried the whole of the activity, the solution being inactive. As an additional precaution, in order to eliminate the possibility of the presence of radioactive nitrogen oxides, the active carbon dioxide was passed into lime water again and treated with I_3^- in alkaline solution. After acidification with sulphuric acid, the carbon dioxide was allowed to react with fresh $\text{Ca}(\text{OH})_2$. This CaCO_3 was radioactive, the recovery being quantitative.

It is probable that the ^{14}C is formed by reaction of the deuterons with the less abundant carbon isotope, ^{13}C , according to the equation



and the yield should accordingly be increased if samples of carbon enriched in ^{13}C are used as targets. Its half-life has not yet been determined, but it is certainly very long.

Preparation of Radiophosphorus

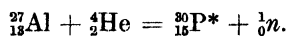
One stable ($A = 31$) and three unstable ($A = 29, 30$, and 32) isotopes of phosphorus are known. Of these, ^{29}P has not been very extensively studied; but ^{30}P (a positron emitter with a half-life of 2.55 min.) possesses historical interest as being one of the first radio-

[†] S. Ruben and M. D. Kamen, *ibid.* 1940, 57, 549.

elements to be prepared. ^{32}P decays by electron emission. Its half-life is 14.3 days.

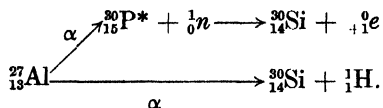
$^{30}\text{P}^*$

The method of preparation given is that used by Curie and Joliot in their original work.† On bombarding aluminium foil with unaccelerated α -particles, these authors observed (in addition to an alternative process leading to a stable silicon isotope) the production of radioactive $^{30}\text{P}^*$ by the reaction course



The product was identified chemically in two ways. In the first place, the irradiated target was dissolved in hydrochloric acid, when the nascent hydrogen, produced by the solution of the residual aluminium foil, converted the phosphorus into radioactive PH_3 , the solution becoming inactive. In the second and more specific method of identification, the irradiated foil was dissolved in an oxidizing acid mixture in order to convert the phosphorus to phosphate. The solution was radioactive. A little inactive phosphate was then added as a carrier, followed by a zirconium salt to precipitate the total phosphate as zirconium phosphate. This precipitate contained the whole of the activity.

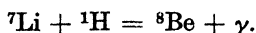
The chemical identification of the element responsible for the activity has to be carried out quickly, since ^{30}P has a half-life of about 3 minutes. It decays by positron emission to the same stable isotope of silicon as is given by the alternative nuclear process which occurs concurrently with the production of ^{30}P , the complete course of the reaction initiated by the bombardment being



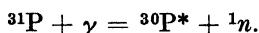
The assignment of the correct mass number (30) to the active phosphorus follows, as usual, partly from mass considerations derived from the most probable equation representing its formation and partly from confirmation based on the production of the same radioactive phosphorus (having the same half-life and other radioactive characteristics) by various cross reactions. Thus $^{30}\text{P}^*$ has, since

† I. Curie and F. Joliot, *Compt. rend.* 1934, **198**, 254; *J. Chim. Physique*, 1934, **31**, 611.

Curie and Joliot's work, been made by bombarding the stable isotope, ^{31}P , with high-energy γ -rays (the nuclear photo-effect). In Bothe and Gentner's work† on the subject, the γ -rays used had an energy of about 17 Mev. and were in general derived from the nuclear reaction



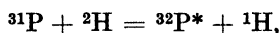
It may be noted that the equivalent mass of these high-energy photons is considerable: thus, on the equivalence of 1 atomic mass unit to 9.32×10^8 e.v., a 17 Mev. photon will have an equivalent mass which is more than 30 times the rest-mass of an electron. Consequently, taking also into consideration the absence of charge, the effectiveness of these high-energy γ -ray photons is not unexpected. In the commonest type of reaction a neutron is ejected from the target, the product being thus isotopic with the target atom but one unit less in mass number. With ^{31}P the reaction is



Other ways of making ^{30}P include the processes $^{32}\text{S}(d, \alpha)^{30}\text{P}$ and $^{30}\text{Si}(p, n)^{30}\text{P}$.‡

$^{32}\text{P}^*$

The following method, involving the reaction



has been used by Newson.§ Red phosphorus was bombarded for an hour with 3-Mev. deuterons. The radioactive product was identified chemically by burning it in a test-tube, dissolving the oxide in water, and boiling with nitric acid to oxidize any unburnt material. Phosphates were then precipitated with magnesia mixture. The precipitate was purified by solution in dilute nitric acid and separated from traces of silica, aluminium, and magnesium by evaporating to dryness (to precipitate the silica, which was inactive), followed by the precipitation of the phosphorus, from dilute nitric acid solution, as ammonium phosphomolybdate. The precipitate contained all the activity. ^{32}P has a half-life of 14.5 days. It decays by β -particle emission, without γ -rays, by the course

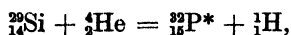
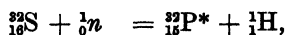
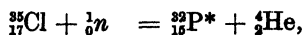


† W. Bothe and W. Gentner, *Naturwiss.* 1937, 25, 90, 126, 191, 224; *Z. Physik*, 1939, 112, 45.

‡ R. Segane, *Phys. Rev.* 1936, 50, 1141; W. H. Barkas, *ibid.* 1939, 56, 287.

§ H. W. Newson, *ibid.* 1937, 51, 624.

All these properties are identical with those of the radiophosphorus made by alternative routes,† such as



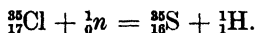
and its mass number, 32, has in this way been established.

Preparation of Radiosulphur

The isotopes of sulphur are 31* (half-life < 10 sec.), 32, 33, 34, 35* (88 days), and 36, the abundances of the stable isotopes, in the order given, being 95.0, 0.74, 4.2, and 0.016 per cent. The better known of the radioactive isotopes is ${}^{35}\text{S}$.

${}^{35}\text{S}^*$

This was made by Andersen‡ by the neutron bombardment of chlorine (as CCl_4 containing a little inactive sulphur as a carrier):



Under the conditions used by Andersen, no active atoms are formed from the carbon of the carbon tetrachloride or, as was shown in check experiments, from sulphur dissolved in carbon disulphide; but the production of some 40-minute chlorine and some 17-day phosphorus (probably ${}^{34}\text{Cl}^*$ (33 min.) and ${}^{32}\text{P}^*$ (14.3 days)) is reported. The active sulphur atoms produced are expelled, and mix with the inactive sulphur carrier.

In order to remove the ${}^{35}\text{S}^*$ from the reaction mixture, the excess of carbon tetrachloride was distilled off and the whole of the sulphur in the residue oxidized to sulphate by treatment with nitric acid and sodium chlorate. This sulphate was precipitated as BaSO_4 in strong hydrochloric acid solution, any phosphate remaining unprecipitated. Alternatively, to obtain a sample of the active sulphur in the free state, Andersen dissolved the residue from the carbon tetrachloride distillation in caustic soda and added hydrochloric acid, when about one-third of the sulphur was precipitated. For measurements of the half-life, samples both of BaSO_4 and of elementary sulphur were made by repeating the purification several times.

The above preparation was confirmed by Levi,§ who states that

† E. Amaldi *et al.*, *Proc. Roy. Soc.* 1934, A 146, 483; H. Fahlenbrach, *Naturwiss.* 1935, 23, 288.

‡ E. B. Andersen, *Z. physikal. Chem.* 1936, B 32, 237.

§ H. Levi, *Nature*, 1940, 145, 588.

the separation of the sulphur is simpler if sodium chloride is taken as the source of the chlorine. Levi used as the neutron source a tube containing 600 mg. of radium together with beryllium, which was placed in the centre of a vessel containing 2 kg. of pure NaCl. After irradiation for 2 months, the salt was dissolved in water and 20 mg. of inactive Na_2SO_4 were added as a carrier. To oxidize the active sulphur, which was present possibly as the element, nitric acid and hydrogen peroxide were added and the solution boiled for several hours. Next, in order to remove active phosphorus, 100 mg. of sodium phosphate were introduced and the phosphorus precipitated by ammonium phosphomolybdate, this being repeated several times until the precipitate showed no signs of activity. Finally, the sulphur was precipitated in the usual way as BaSO_4 .

$^{35}\text{S}^*$ has also been made by the action of deuterons (from the Berkeley cyclotron) on inactive sulphur.†

The radiation from ^{35}S consists of very soft β -rays of a maximum energy of 0.1–0.2 Mev. and for this reason the measurement of its half-life has to be made with a Geiger counter or similar instrument provided with an especially thin mica window. It has a half-life of about 88 days; and it is of importance as a tracer.

Preparation of Radiobromine

Like radiosulphur, radioactive forms of all the halogens are of considerable importance on account of the wide use to which they have been put as tracers. A list of the mass numbers of the known halogen isotopes (save those of fluorine, which have already been included in Table 76), together with the percentage abundances of the stable isotopes and the half-lives and type of decay of the active isotopes,‡ is given in Table 77.

TABLE 77

<i>Chlorine</i>	<i>Bromine</i>	<i>Iodine</i>
33* (2.8 sec.)	78* (β^+ , γ ; 6.4 min.)	124* (β^+ ; 4 days)
34* (β^+ ; 33 min.)	79 (Stable; 50.6)	126* (β^- , γ ; 13 days)
35 (Stable; 75.4)	80* (γ ; 4.4 hr.)	127 (Stable, 100)
36* (β^+ , K , β^- ; > 1 yr.)	80* (β^- , γ ; 18 min.)	128* (β^- , γ ; 25 min.)
37 (Stable; 24.6)	81 (Stable; 49.4)	130* (β^- , γ ; 12.6 hr.)
38* (β^- , γ ; 37 min.)	82* (β^- , γ ; 34 hr.)	131* (β^- , γ ; 8 days)
	83* (β^- ; 140 min.)	

† H. H. Voge, *J. Amer. Chem. Soc.* 1939, **61**, 1032; J. L. Tuck, *J. Chem. Soc.* 1939, 1293.

‡ G. T. Seaborg, loc. cit.

Of these halogens, bromine is of special interest, since this element gave the first known example of radio-isomerism. The bromine isotopes, moreover, form a suitable group for illustrating the methods of cross checking which are used for assigning mass numbers; and the group will accordingly be considered specially from this standpoint rather than from that of chemical identification only.

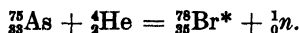
In order to follow the reasoning used, it will be convenient first to tabulate the mass numbers of the immediate neighbours of bromine (which are used as targets) and also to refer back to Table 74, which gives the effect of various reaction types on Z and A .

TABLE 78

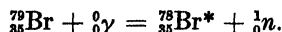
Element	As	Se	Br	Kr	Rb
Atomic No.	33	34	35	36	37
Isotopic mass numbers and abundances	75 (100%)	74 (0.9%) 76 (9.5%) 77 (8.3%) 78 (24%) 80 (48%) 82 (9.3%)	79 (50.6%) 81 (49.4%)	78 (0.35%) 80 (2.01%) 82 (11.5%) 83 (11.5%) 84 (57.1%) 86 (17.5%)	85 (72.8%) 87 (27.2%)

$^{78}\text{Br}^*$ (6.4 min., β^+)

On irradiating arsenic with a beam of 11-Mev. α -particles from the Berkeley cyclotron, Snell† obtained a 6.4-min. activity which followed the chemistry of bromine. Since the probable nuclear reaction types are either α, n or α, p under the conditions used, and since an α, p reaction would lead to an isotope of selenium rather than to bromine, the most probable process (the isotopic starting-point of which is simplified by the fact that natural arsenic, used as the target, consists of a single isotope, ^{75}As) is



This assignment of the 6.4-min. positron activity to ^{78}Br is confirmed by the production of the same bromine activity‡ by irradiating bromine with γ -rays under conditions under which a γ, n reaction would be expected:§

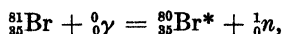


† A. H. Snell, *Phys. Rev.* 1937, **52**, 1007.

‡ W. Y. Chang, M. Goldhaber, and R. Segane, *Nature*, 1937, **139**, 162.

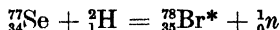
§ See W. Bothe and W. Gentner, *Naturwiss.* 1937, **25**, 90, 126, 191, 284; *Z. Physik*, 1939, **112**, 45.

The similar reaction of the other stable bromine isotope ^{81}Br ,

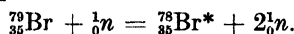


was also observed by Bothe and Gentner and will be referred to under ^{80}Br .

Other methods of making ^{78}Br include the bombardment of selenium with high-energy deuterons, when the d, n reaction



occurs. This preparation was successfully used by Snell. ^{78}Br has also been made by bombarding bromine with fast neutrons,† when a $n, 2n$ process takes place:



^{78}Br decays, by positron emission, to ^{78}Se .

$^{80}\text{Br}^*$ and $^{82}\text{Br}^*$

In addition to the 6.4-min. positron activity, three simultaneously produced negative β -activities, having half-lives of 18 minutes, $4\frac{1}{2}$ hours, and 34 hours and all following the chemistry of bromine, were obtained by a number of workers‡ by bombarding natural bromine either with neutrons or with deuterons, the three activities being obtained with each of these projectiles.

The occurrence of two stable bromine isotopes only (79 and 81) in the natural element was checked mass-spectroscopically by Blewett§ under conditions which would have detected 1 part in 30,000 of any other isotope; and the apparent anomaly, which was explained by Snell by the now generally accepted conception of radio-isomerism, accordingly lay in the persistent formation of three radioactive products where two only (one from each of the stable isotopes) would be expected.

Snell obtained the three activities (18 min., $4\frac{1}{2}$ hrs., and 34 hrs.) by the deuteron bombardment of bromine. Kourchatow obtained the same activities by neutron bombardment. In each case it was probable, from experience based on other deuteron or neutron reactions, that any radioactive isotopes formed would be in the immediate neighbourhood of the stable isotopes (79 and 81) in the bromine forming the target. The formation of $^{78}\text{Br}^*$ (which was actually

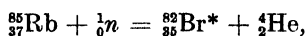
† F. A. Heyn, *Nature*, 1937, **139**, 842.

‡ B. Kourchatow, I. Kourchatow, L. Myssowsky, and L. Roussinow, *Compt. rend.* 1935, **200**, 1201; A. H. Snell, loc. cit.; E. Amaldi et al., *Proc. Roy. Soc.* 1934, **A 146**, 483; C. H. Johnson and F. T. Hamblin, *Nature*, 1936, **138**, 504.

§ J. P. Blewett, *Phys. Rev.* 1936, **49**, 900.

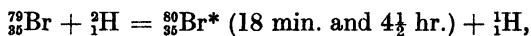
suggested by some authors, who postulated a $n, 2n$ process for the neutron bombardment) was ruled out, since ^{78}Br is known to be a positron emitter. ^{79}Br and ^{81}Br , the mass numbers of which have been fixed mass-spectroscopically, are stable; and $^{83}\text{Br}^*$ (see next section) has a half-life of 140 minutes. Accordingly, the only vacant mass numbers in the range are 80 and 82, which have to be filled by *three* isotopes, corresponding with the three given half-lives.

It was observed, further, that the 34-hr. bromine activity could be obtained, without the 18-min. and $4\frac{1}{2}$ -hr. activities, from an element of considerably higher atomic and mass numbers, namely rubidium, by a fast neutron reaction which is probably

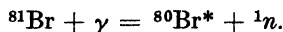


from which it seemed probable, firstly, that this 34-hr. activity is due to a single bromine isotope and, secondly, that it should be ascribed to the higher of the vacant mass numbers (82).

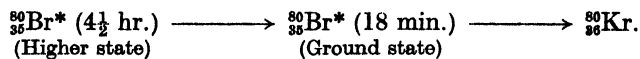
On the basis of considerations of this nature, as well as from a study of the relative strengths of the three activities induced in bromine by different methods, Snell allocated the 34-hr. activity to ^{82}Br and *both* of the 18-min. and the $4\frac{1}{2}$ -hr. activities to ^{80}Br , the reactions (for deuteron bombardment) leading to these being



This ascription of both the 18-min. and the $4\frac{1}{2}$ -hr. periods to ^{80}Br is further confirmed by the production of these by the photo-nuclear reaction (Bothe and Gentner)



It was found that, of the radio-isomers, the $4\frac{1}{2}$ -hr. entity is that possessing the higher energy, the course of the decay being

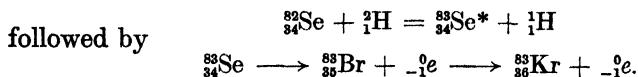


$^{83}\text{Br}^*$ (140 min., β^-)

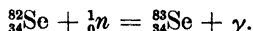
This isotope is formed, together with ^{78}Br and some ^{82}Br , by the action of deuterons on selenium. It was first recognized by Snell who, on irradiating selenium with deuterons from the Berkeley cyclotron for a short period (5 min.), observed, in addition to the ^{78}Br activity (6.4 min.), a new bromine activity of about $2\frac{1}{2}$ hours. With longer exposures, if the target was allowed to stand until most of the 6.4-min. activity had disappeared, the $2\frac{1}{2}$ -hr. period, with the

chemistry of bromine, was again clearly recognized and the presence also of some 34-hr. ^{82}Br was detected.

Snell considers that the $4\frac{1}{2}$ -hr. bromine is not formed directly from ^{82}Se by the d, n reaction, $^{82}\text{Se}(d, n)^{83}\text{Br}$, but by the intermediate formation of an unstable selenium isotope, ^{83}Se , which then decays by β -particle emission, the course being



Evidence for this course was obtained by the observation of a radioactive process in the selenium fraction derived from the experiments. The reaction series, $^{83}\text{Se} \rightarrow {}^{83}\text{Br} \rightarrow {}^{83}\text{Kr}$, has also been studied by Langsdorf and Segrè,[†] who prepared the $^{83}\text{Se}^*$ by irradiating selenium with slow neutrons according to the process



These authors give the half-life of ^{83}Se as about 30 minutes and that of ^{83}Br (which was separated as AgBr) as 140 minutes. As a result of their analysis of activity also in the krypton fraction, Langsdorf and Segrè consider that the ^{83}Kr produced in the first instance is a radio-isomer of ordinary stable ^{83}Kr .

It may be noted that ^{83}Br , with its characteristic period, has also been detected in the fission products of thorium.[‡]

USES OF ARTIFICIAL RADIO-ELEMENTS

1. *Determination of the Properties of Unknown Natural Elements*

Since all isotopes of a given element—irrespective of whether they are stable or radioactive—have the same chemical properties, it follows that, if an element is unknown or insufficiently known in the natural state but can be made artificially, this artificial element can be used for the determination of these properties.

The definite isolation, from natural sources, of the following three elements:

- (a) Element 61 (a rare earth element lying between neodymium and samarium),
- (b) Element 85 (eka-iodine),
- (c) Element 87 (eka-caesium),

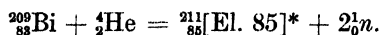
probably still requires further work. In addition, the possibility of the existence of elements beyond uranium ($Z = 92$) also arises.

[†] A. Langsdorf and E. Segrè, *Phys. Rev.* 1940, **57**, 105.

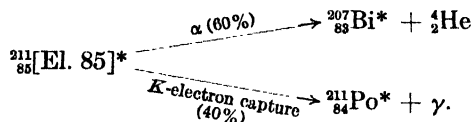
[‡] E. Bretscher and L. G. Cook, *Nature*, 1939, **143**, 559.

In the present section, the determination of the properties of Element 85 on the basis of an artificially prepared isotope will be considered. It should be noted that this element lies in the extreme range of atomic numbers, in which only radioactive isotopes may be capable of existence. This alone, however, does not preclude its eventual isolation also from natural sources (cf. Po, Ra, etc.).

Element 85. Corson, Mackenzie, and Segrè,[†] on bombarding bismuth with high-energy (32-Mev.) α -particles, observed a reaction which is probably



The resulting radio-element had a half-life of about 7.5 hours and appeared to undergo a branching decay either to ^{207}Bi by loss of an α -particle or to ^{211}Po by K -electron capture:



Since Element 85 should be a homologue of iodine, it appeared probable that it would be volatile; and it was actually found that the activity in question could, by heating the bombarded target to the melting-point of bismuth, be distilled off and collected on a water-cooled plate.

Its chemical properties are of great interest, since it appears to resemble a heavy metal rather than a halogen. Thus it is not, in the presence of an iodide as a carrier, precipitated as an insoluble silver salt from dilute nitric acid. Sometimes there is a slight entrainment of the activity by the silver iodide; but further purification gives inactive silver iodide. It is also not precipitated, as an insoluble lead or thallous salt, by adding hydrochloric acid to a solution of the element in the presence of lead or thallous salts.

On the other hand, it can be quantitatively precipitated from its solutions by hydrogen sulphide in the presence of suitable sulphide carriers such as bismuth, mercury, silver, or antimony salts. Its coprecipitation as an insoluble hydroxide by adding sodium hydroxide, in the presence of mercury, iron, or other salts, is, however, incomplete and is probably due to adsorption.

Reducing agents (sulphur dioxide, zinc, stannous chloride, etc.)

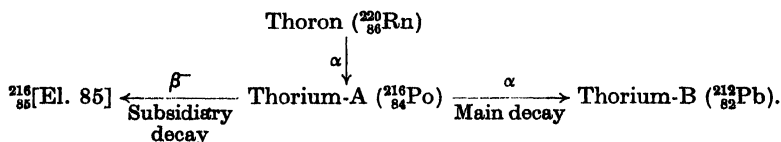
[†] D. R. Corson, K. R. MacKenzie, and E. Segrè, *Phys. Rev.* 1940, **58**, 459, 672, 1087.

precipitate Element 85 quantitatively; and its precipitation with sulphur dioxide in 3N-hydrochloric acid has been used by Corson, Mackenzie, and Segrè for its separation from polonium, which remains in solution. It was also deposited on a copper plate from a 0.25N-nitric acid solution containing bismuth and mercury; and, by heating the plate cautiously, the mercury, which is also deposited, could be distilled off before Element 85 begins to distil.

As has already been mentioned, all these properties, with the exception of the volatility at high temperatures, suggest that the element obtained by Corson, MacKenzie, and Segrè possesses the characteristics of a metal rather than those of a halogen. It should be noted, as these authors clearly recognize in their papers, that the identity of their product with an element of atomic number 85 has not yet been established with complete certainty, although this is highly probable from its method of formation.

The spontaneous formation of another radioactive isotope of Element 85 has been claimed by Minder† on the basis that the initial increase in β -radiation of radium emanation with the time is greater than that which would be expected if only the normal products, Ra-B and Ra-C, are formed; but later work by Karlik and Bernert‡ throw doubt on this, and the occurrence of Element 85 in the radium series accordingly requires confirmation.

In a later paper Leigh-Smith and Minder§ claim the probable formation of Element 85 as a branch product of the disintegration of thorium-A, on the basis of the probability, expressed by Turner,|| that thorium-A, in addition to its main change to thorium-B, is also to a slight degree β -active. The process, starting with thorium emanation (thoron), would thus be:



The elements with which the various stages are isotopic are given by the symbols in brackets. Like the previously discussed isotope, $^{211}_{85}[\text{El. 85}]$, this further isotope is volatile and was separated by

† W. Minder, *Helv. Phys. Acta*, 1940, 13, 144.

‡ B. Karlik and T. Bernert, *Naturwiss.* 1942, 30, 685.

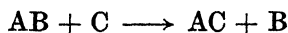
§ A. Leigh-Smith and W. Minder, *Nature*, 1942, 150, 767.

|| L. A. Turner, *Phys. Rev.* 1940, 57, 950.

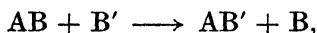
sublimation, at 180° , on to a cooled silver wire. It decays by electron emission to a gaseous emanation, $^{218}_{86}\text{Rn}$, isotopic with thorium emanation and with radon.

2. *Detection of Exchange Processes*

While a reaction such as



can be investigated by ordinary means, the corresponding exchange process



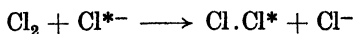
in which B and B' are distinct individual atoms of the same element, can, as has already been discussed on p. 106, only be detected if these two individual atoms can be distinguished from one another by some form of label.

In general, two methods of labelling are available, both involving the use of different isotopes for B and B'. Firstly, if B and B' differ sufficiently in mass, the exchange can in suitable circumstances be followed by, for instance, density measurements. This method has been widely used for hydrogen-deuterium exchange (see Chapter II) and it has to a very limited extent been used for other elements; but, save in the special case of deuterium and hydrogen—which, however, differ so much in mass that intensity differences in chemical properties are also involved—the mass differences are too small to permit great accuracy; and highly refined methods are usually required for the detection of any density differences which result.

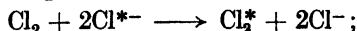
The employment, on the other hand, of a radio-element either for B or B' allows exchange to be detected very easily by reason of the transfer of the characteristic radioactivity: further, since radioactive isotopes of convenient (not too short) life are in general available throughout the periodic system, this method of labelling greatly extends the practical possibility of studying exchange. Where exchange takes place, this can be followed by measuring the encroachment of the radioactivity on the previously inactive part of the system (for instance by determining radioactive intensities by means of a Geiger counter); and, by working in this way, it has been shown that exchange processes are far more common than was formerly supposed. A short description of some of the reactions which have been studied in this way is given below.

Halogen Exchange. Rapid exchange occurs between a free halogen

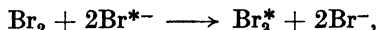
and a radioactive halide ion in aqueous solution. This was observed by Long and Olson† for inactive chlorine in the presence of a solution of radioactive NaCl^* , the exchange process being



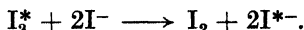
or



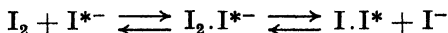
similarly, Dodson and Fowler‡ found a rapid exchange for



and Hull, Shiflett, and Lind§ found a free exchange between radioactive iodine and inactive iodide:



These authors postulate a mechanism of the type



for the exchange between iodine and an iodide; and Dodson and Fowler give a similar mechanism for the bromine-bromide exchange, but the following of such a path by chlorine is less obvious.

In order to follow all these exchanges, the free halogen, after the exchange, was separated from the aqueous solution, for instance by repeatedly shaking this with an immiscible organic solvent, the distribution of the activity being determined by converting each form of the halogen (i.e. the halide ion remaining in the aqueous solvent and the free halogen from the organic solvent) into the silver halide, following which the activity of the halide from each source was measured. Exchange also occurs in non-ionizing solvents. Thus Topley and Weiss|| found that exchange between radioactive bromine and a solution of HBr in carbon tetrachloride was complete in less than 2 minutes.

Exchanges between the halogens of phosphorus halides (PCl_3 , PBr_3 , PCl_5 , and PBr_5) and radioactive halogens in carbon tetrachloride solution—which is itself inert—at room temperature have been studied by Koskosky and Fowler.¶ The partition of the radioelement takes place rapidly in all cases; and Koskosky and Fowler conclude that all the halogen atoms in the pentahalides are equally

† F. A. Long and A. R. Olson, *J. Amer. Chem. Soc.* 1936, **58**, 2214.

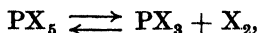
‡ R. W. Dodson and R. D. Fowler, *ibid.* 1939, **61**, 1215; A. V. Grosse and M. S. Agruss, *ibid.* 1935, **57**, 591; S. Roginsky and N. Gopstein, *Phys. Z. Sovietunion*, 1935, **7**, 672.

§ D. E. Hull, C. H. Shiflett, and S. C. Lind, *J. Amer. Chem. Soc.* 1936, **58**, 535.

|| B. Topley and J. Weiss, *J. Chem. Soc.* 1936, 912.

¶ W. Koskosky and R. D. Fowler, *J. Amer. Chem. Soc.* 1942, **64**, 850.

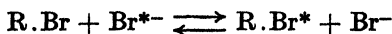
reactive and equivalent. This result is of interest, since the pentahalides are known to be dissociated in solution according to the course



the pentabromide being dissociated to a greater extent, under comparable conditions, than the pentachloride. The exchange is considered to proceed by virtue of this equilibrium; and, if the five phosphorus-halogen bonds were not equivalent, it might be expected, as an extreme case, that complete exchange with two halogen atoms of the pentahalide might occur and little or none with the other three or, at any rate, that two of the halogen atoms would exchange at a different rate from the other three. This equivalence of all five phosphorus-halogen bonds agrees with the views of Pauling and others of the presence in PCl_5 of five equivalent hybrid (probably dsp^3) covalent bonds, which, from bond-length measurements, seem to have some double-bond character and may also be slightly ionic.

The degree of exchange of the covalently linked halogen atoms in an organic halide depends greatly on the conditions. In general, little or no exchange occurs. This absence of exchange was observed, for instance, by Hull, Shiflett, and Lind for the systems, $I_2^* + CH_3I$ and $I_2^* + CHI_3$, also by Liberatore and Wiig† for mixtures of Br_2^* and C_2H_5Br ; and the non-exchangeability of organic halides generally, either alone or in non-ionizing solvents, has been confirmed by a number of other workers.

On the other hand, some measure of replacement will obviously take place if the conditions (high temperatures or the presence of ionizing solvents) are such that a kinetic thermal or ionic equilibrium is set up. Thus, Tuck‡ found that a radioactive iodide ion exchanged with the iodine atom of tertiary butyl iodide in liquid sulphur dioxide solution; and he employed the method to determine the velocity of electrolytic dissociation of butyl iodide. This dissociation also occurred in acetone and in methyl alcohol, but at rates about 100 and 200 times slower than in sulphur dioxide. No exchange was obtained with iodobenzene in liquid sulphur dioxide; but benzyl iodide behaved in much the same way as butyl iodide. The velocity and kinetics of the exchange reaction



† L. C. Liberatore and E. O. Wiig, *J. Chem. Phys.* 1940, **8**, 349.

‡ J. L. Tuck, *Trans. Faraday Soc.* 1937, **34**, 222.

in a solvent consisting of 90 per cent. acetone and 10 per cent. of water have been measured by le Roux and Sugden† and by Elliott and Sugden‡ for *n*-butyl bromide, isobutyl bromide, *n*-propyl bromide, and isopropyl bromide.

A type of exchange process which is due to a kinetic oxidation-reduction equilibrium or, more generally, to an electron-transfer equilibrium is also common. This may be illustrated by exchange processes with oxygenated halogen ions. While no exchange takes place between chlorate, bromate, or iodate ions and the corresponding halogen in neutral solution, exchange does occur if the solution is acidified.§ The action of strong sulphuric acid in inducing exchange between radioactive iodine and an iodate ion was also noticed by Hull, Shiflett, and Lind, who attributed the effect to the presence, in sulphuric acid solution, of a kinetic oxidation-reduction equilibrium. This view is also taken by later authors; and other examples of the effect will be given below.

Exchanges involving Sulphur, Phosphorus, etc. As with the halogens, covalently linked sulphur is, at the ordinary temperature, in most cases too firmly bound to allow any appreciable degree of exchange. Cooley, Yost, and McMillan|| have studied the exchange of elementary sulphur with the sulphur in carbon disulphide. A solution of radioactive sulphur in the disulphide was heated to 100° in a sealed tube for periods up to about 70 hours, after which the carbon disulphide was distilled off at a low temperature (in order to avoid the possible volatilization of the sulphur) into a receiver cooled in liquid air. Both the distillate and the residual sulphur were subjected to a Carius combustion, and the resulting sulphuric acid was converted into barium sulphate. No activity was observed in any of the sulphur preparations derived from the originally inactive carbon disulphide, showing that no measurable exchange between the radioactive sulphur and the carbon disulphide had occurred. The exchangeability of the sulphur in substances such as $(C_2H_5)_2S$ or in thiophen does not appear to have been determined.

Stable oxygenated ions containing sulphur also do not in most cases

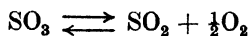
† L. J. le Roux and S. Sugden, *J. Chem. Soc.* 1939, 1279.

‡ G. A. Elliott and S. Sugden, *ibid.*, p. 1836.

§ W. F. Libby, *J. Amer. Chem. Soc.* 1940, **62**, 1930; O. D'Agostino, *Gazz.* 1935, **65**, 1071.

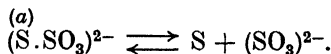
|| R. A. Cooley, D. M. Yost, and E. McMillan, *J. Amer. Chem. Soc.* 1939, **61**, 2970.

exchange readily. Thus, Voge and Libby† found no exchange in solution between $(S)^{2-}$ and $(S^*O_4)^{2-}$ or between $(SO_3)^{2-}$ and $(S^*O_4)^{2-}$. Further, there is no sulphur exchange between sulphur dioxide and sulphur trioxide in the gas phase unless the mixture is heated to a temperature at which the dissociation



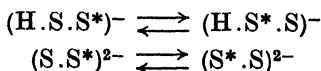
is appreciable, when sulphur exchange takes place. This gas-phase exchange also occurs at 280° and above in the presence of a platinum catalyst.

The case of the thiosulphate ion is exceptional, probably on account of the labile nature of the S—S bond and the existence of the equilibrium



This should render the sulphur atom marked (a) susceptible to exchange; but the exchange does not seem to penetrate appreciably into the stable sulphite ion. Evidence on this point is to be found in the work of Andersen,‡ who prepared sodium thiosulphate containing the ion $(S^*.SO_3)^{2-}$ by adding radioactive sulphur to inactive sodium sulphite. The solution was then acidified with hydrochloric acid to precipitate the thiosulphate sulphur and to generate sulphur dioxide from the sulphite sulphur. The activity was almost entirely confined to the precipitated sulphur, the sulphur dioxide, after oxidation to sulphuric acid with hydrogen peroxide and precipitation as barium sulphate, being almost inactive.

It may be noted that, in the somewhat analogous case of a polysulphide, the exchange represented by the transposition of the sulphur atoms according to the equation



occurs freely owing to the simplicity of the ions and to their similarity save in the location of the charge. Voge and Libby§ added radioactive sulphur to an oxygen-free solution of ammonium sulphide, the solution being then heated to 100° until the sulphur had dissolved. On acidifying, the persulphide sulphur was precipitated and the

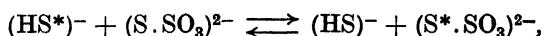
† H. H. Voge and W. F. Libby, *J. Amer. Chem. Soc.* 1937, **59**, 2474; W. F. Libby, *ibid.* 1939, **61**, 1032.

‡ E. B. Andersen, *Z. physikal. Chem.* 1936, **B 32**, 340.

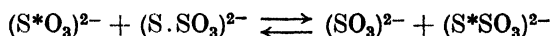
§ H. H. Voge and W. F. Libby, *loc. cit.*

normal sulphide sulphur was evolved as hydrogen sulphide. The precipitated sulphur was oxidized to sulphuric acid and precipitated as barium sulphate. The hydrogen sulphide was absorbed in lead acetate. Both forms of sulphur were radioactive.

By virtue of this polysulphide exchange and of the labile nature of the external sulphur atom in the thiosulphate ion, exchange occurs, in aqueous solution, between sulphides and thiosulphates,



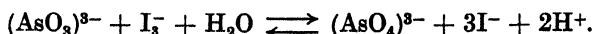
but it is not very fast. Voge and Libby state that, under their conditions, it was complete in 100 hours at 100°. The rate of exchange between a sulphite and a thiosulphate,



is, on the other hand, much greater than that of the sulphide-thio-sulphate reaction, probably on account of the greater degree of kinetic activity in the equilibrium involved.

The behaviour of phosphorus in stable oxygenated ions resembles that of sulphur in systems in which there is no appreciable oxidation-reduction or other kinetic equilibrium. Wilson† found that there was no appreciable exchange between phosphorous and radioactive phosphoric ions either in acid or in alkaline solution: further, Perrier and Segrè‡ observed no exchange between a radioactive phosphate (containing $^{32}\text{P}^*$) and an inactive hypophosphite even after 10 days at room temperature followed by 24 hours at 100°. The method of separation was much the same in both cases. Perrier and Segrè first removed the phosphate from the solution by precipitation as calcium phosphate. The hypophosphite was then oxidized to phosphate by iodine and hydrogen peroxide and removed similarly. This latter calcium phosphate was inactive, save in cases in which the first precipitation had been incomplete.

Similarly, exchange does not take place§ with measurable velocity between a radioactive arsenite and an inactive arsenate either in dilute acid or alkaline solution. On adding iodine, however, exchange occurs. Wilson and Dickinson assume that this proceeds by the oxidation and reduction of the arsenic according to the equation,

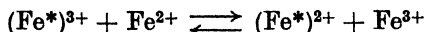


† J. N. Wilson, *J. Amer. Chem. Soc.* 1938, **60**, 2697.

‡ C. Perrier and E. Segrè, *Ricerca Sci.* 1938, **9**, 638.

§ J. N. Wilson and R. G. Dickinson, *J. Amer. Chem. Soc.* 1937, **59**, 1358.

Exchanges involving Metallic Ions. Where an active kinetic oxidation-reduction equilibrium, in the sense of a balance between two metallic ions of different valencies, exists in a solution, a free transition may occur in the valency of an individual ion. Thus, Kennedy, Ruben, and Seaborg† state that exchange between ferrous and ferric ions, in an equilibrium of the type,



occurs instantaneously (in less than 10 sec.), the radioactivity originally confined to one valency form of the ion being distributed between both forms. Mercurous and mercuric ions exchange similarly.

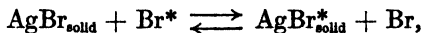
In the case of ions in which the metal is bound covalently as a member of a complex, exchange at an appreciable rate does not take place. Accordingly, no exchange was noted between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$.

DETERMINATION OF SPECIFIC SURFACE

Paneth's radioactive method‡ for the determination of the surface of finely divided solids can obviously be greatly extended in virtue of the far wider choice of radioactive elements which is possible if artificial elements are used.

The method may be illustrated by the determination, by Kolthoff and his co-workers,§ of the relative surfaces of various specimens either of freshly precipitated lead sulphate by using radioactive lead or of silver bromide with a solution containing radioactive bromine.

In both cases the exchange process reached an equilibrium so rapidly that it was almost certain that only the external surface, including possibly crevices, took part in the exchange. For the system



this equilibrium corresponds with the relationship,

$$\frac{\text{Br}^* \text{ on surface}}{\text{Br}^* \text{ in solution}} = \frac{\text{Br on surface}}{\text{Br in solution}}.$$

The ratio on the left of the above equation can be obtained by measuring the relative radioactive intensities of the solid and of the

† See G. T. Seaborg, *Chem. Rev.* 1940, **27**, 256.

‡ F. Paneth, *Phys. Z.* 1915, **15**, 924; *Z. Elektrochem.* 1922, **28**, 113.

§ I. M. Kolthoff and H. C. Yutzy, *J. Amer. Chem. Soc.* 1937, **59**, 1634; I. M. Kolthoff and A. S. O'Brien, *ibid.* 1939, **61**, 3409, 3414.

solution; and, from this, since only a small percentage of radioactive bromine was present and since

$$\text{Br}_{\text{surface}} = \frac{\text{Br}_{\text{surface}}^*}{\text{Br}_{\text{solution}}^*} \cdot \text{Br}_{\text{solution}} = R \cdot \text{Br}_{\text{solution}},$$

the relative surface of a number of specimens of silver bromide (or the change in surface of a single specimen with 'ageing') could be calculated. The method was compared, as has also been done by Paneth, with the determination of relative surfaces by the absorption of dyes, which—probably owing to the larger size of the dye molecule—in general gave a smaller apparent surface.

VIII

URANIUM AND THE TRANSURANIC ELEMENTS

URANIUM has always possessed a special interest as the end element in the classical periodic system; and this interest has recently been greatly intensified by the preparation of elements beyond the previously accepted limit of atomic number and by the utilization of uranium and its immediate neighbours in a new type of nuclear reaction involving the splitting of the nucleus.

The subject-matter of the present chapter falls naturally into two sections, namely into a short recapitulation of what is generally known with regard to the preparation and properties of the new elements and especially of their relationship to uranium and, secondly, into a summary of published knowledge with regard to nuclear fission.

TRANSURANIC ELEMENTS

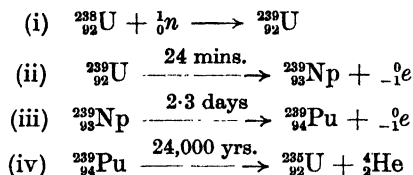
Elements 93 and 94 (Neptunium and Plutonium)

While most of the reputed transuranic elements which were at one time thought to be produced by the bombardment of uranium with neutrons have now been shown to be fission products, it has been established that neutrons of certain energies, which probably represent nuclear resonance values, may be captured by uranium without inducing fission. The published knowledge† of this important reaction and of the known properties of the products may be summarized as follows.

The first product of the capture of a neutron by the most common uranium isotope, ^{238}U , appears to be a higher isotope, ^{239}U , which then undergoes β -decay, with a half-life of about 24 minutes, to an active isotope of Element 93. This, in turn, emits a further β -particle, passing to a long-lived isotope of Element 94 which, by α -particle

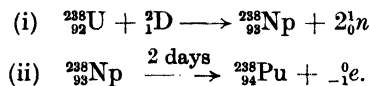
† E. McMillan, *Phys. Rev.* 1939, **55**, 510; E. McMillan and P. H. Abelson, *ibid.* 1940, **57**, 1185; E. T. Booth, J. R. Dunning, A. V. Grosse, and A. O. Nier, *ibid.* 1940, **58**, 475; F. Strassmann and O. Hahn, *Naturwiss.* 1942, **30**, 256; *Brit. Chem. Abstracts*, 1942, A 1, 374; K. Starke, *Naturwiss.* 1942, **30**, 107; *Brit. Chem. Abstracts*, 1942, A 1, 256. See also G. T. Seaborg, *Chem. Reviews*, 1940, **27**, especially p. 269; H. D. Smyth, *Atomic Energy*, United States Government Printing Office and H.M. Stationery Office, London, 1945; L. S. Foster, *J. Chem. Education*, 1945, **22**, 619; G. T. Seaborg, *Chem. and Eng. News*, 1945, **23**, 2190.

emission, eventually reverts to a lower uranium isotope. These changes may be represented by the equations:

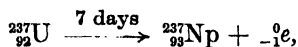


in which the symbols Np and Pu denote the elements neptunium and plutonium.

Other isotopes both of neptunium and of plutonium are also known. Thus ${}^{238}\text{Np}$, which decays to ${}^{238}\text{Pu}$, was made by McMillan and Abelson by bombarding uranium for long periods with deuterons from the Berkeley cyclotron, the reaction being:



Seaborg states that a still lower neptunium isotope, ${}^{237}\text{Np}$, is formed by the β -decay of the artificial uranium isotope, ${}^{237}\text{U}$,



the uranium isotope being made by a $n, 2n$ reaction from ${}^{238}\text{U}$. This neptunium isotope, which is an α -emitter, has a very long half-life (2.25×10^6 years) and is, therefore, suitable for the study of the chemical properties.

It may be noted that plutonium, probably as ${}^{239}\text{Pu}$, has been shown by Seaborg and Perlman† to occur naturally in very small concentrations in pitchblende, in which it is presumably formed continuously by the non-fissional absorption by the ${}^{238}\text{U}$ of some of the neutrons which are always present and which may result, for instance, from the spontaneous fission of ${}^{238}\text{U}$. The plutonium content of such uranium ores has been estimated by these workers as being of the order of 1 part in 10^{14} . The plutonium thus formed of course undergoes continuous decay with the half-life already given.

Chemical Properties of Neptunium and Plutonium

Neptunium, from its logical position in the extrapolated periodic system, might perhaps be expected to be a homologue of rhenium. Actually it has few of the properties of rhenium: thus it is not

† Cited by G. T. Seaborg, *Chem. and Eng. News*, 1945, **23**, 2192.

precipitated by hydrogen sulphide in acid solution, although it is stated to be precipitated by ammonium sulphide; and it does not form an oxide which is volatile at a red heat.

Neptunium is, however, very similar to uranium. This is shown, for instance, in its co-precipitation with this element as sodium uranyl acetate, which is a characteristic reaction of uranium. In a lower oxidation state, it also shows a great similarity to the tetravalent rare earths; but it can be separated from these by taking advantage of its passage into a higher oxidation state in the presence of a suitable oxidant. McMillan and Abelson have summarized its principal points of difference from the rare earths.† Thus, although neptunium in a lower valency state (i.e. in the presence of sulphur dioxide) is precipitated quantitatively with a cerium carrier by adding hydrogen fluoride, it is not co-precipitated by this reagent in the presence of an oxidizing agent such as a bromate in strong acid. These and other reactions show that, in a higher state, it loses its resemblance to the rare earths; and it is, on the other hand, particularly in a higher oxidized state that it exhibits the specially pronounced similarity to uranium.

The separation of Element 93 from uranium has been discussed by Strassmann and Hahn, who state that it is not precipitated by oxine (8-hydroxyquinoline) and suggest the use of this property as a separation method. These authors also give some additional properties. It is, both in an oxidized and in a reduced state, completely precipitated by ammonia, but it is only partly precipitated from hydrochloric acid solution by ammonium oxalate or ammonium tartrate.

Neptunium was shown by McMillan and Abelson to be capable of existence in at least two oxidation states, namely a possibly tetravalent state corresponding with U^{4+} or Th^{4+} and a hexavalent state corresponding with uranium in the uranyl compounds or in the uranates. Later work, cited by Seaborg and carried out with ^{237}Np , has shown that four oxidation states exist, corresponding with valencies of III, IV, V, and VI, with a general shift in stability towards the lower oxidation states. This tendency, which was also noticed by McMillan and Abelson, is in the opposite direction to that in the uranium compounds, in which the trivalent state is the least stable and the hexavalent state the most stable. Accordingly, in general, reagents of greater oxidizing power, or more energetic oxidizing

† See also E. Segrè, *Phys. Rev.* 1939, **55**, 1104.

conditions, are required to oxidize neptunium from a lower to a higher state than is the case for uranium.

Although plutonium and a large number of its compounds have been successfully prepared and their properties examined, only the barest outline of these properties has up to the present been published. Like neptunium, it is known to resemble uranium and, also like neptunium, it is stated† to be capable of existence in four states of oxidation corresponding with positive valencies of III, IV, V, and VI. According to Seaborg, the lower oxidation states tend to be more stable than is the case for neptunium. In its highest oxidation state,‡ plutonium forms the positive radical, $(\text{PuO}_2)^{2+}$, which may be compared with the uranyl radical, $(\text{UO}_2)^{2+}$. Thus, both plutonium and neptunium are similar in chemical properties to uranium, with an increase in stability of the lower oxidation states in going towards plutonium.

Elements 95 and 96

The production of two further transuranic elements having the above atomic numbers has recently been reported.§ These were obtained by G. T. Seaborg, R. A. James, L. O. Morgan, and A. Ghiorso by bombarding ^{238}U and ^{239}Pu with high-energy (40 Mev.) helium ions in the rebuilt Berkeley cyclotron; and their properties have been studied by tracer methods. Details of these have not yet been published, but the fundamental importance of this further extension to the periodic system needs no emphasis.

Probability of a Heavy-Element Transition Series

On the basis of the very close resemblance of neptunium to uranium, McMillan and Abelson suggested that neptunium may be the second member of a heavy-element 'rare earth' series starting with uranium. Plutonium obviously continues this series. The subject has recently been discussed by Seaborg,§ who suggests that the elements in question may form part of a transition series beginning not with uranium but with actinium. Seaborg calls this series the actinide series from an analogy to the lanthanide series which includes the rare earths and considers that, in the actinide series, the

† H. D. Smyth, op. cit., p. 61.

‡ L. S. Foster, loc. cit.

§ See G. T. Seaborg, *Chem. and Eng. News*, 1945, 23, 2192.

5*f* electronic shell may be progressively filled in a similar way to the filling of the 4*f* shell in the lanthanide series.

Seaborg's interesting conception seems certainly to be true in the sense that a transition series is merely one in which an internal shell is being filled; but, although the properties of some of the immediate precursors of uranium, particularly those of actinium and protoactinium, are still imperfectly known, it would appear that a specially close degree of similarity begins with uranium and extends, as far as can be seen from published papers, into the transuranic elements. The properties of actinium, thorium, and protoactinium are moreover in general agreement with the hitherto accepted filling of an outer (6*d*) shell which is sufficiently near in position and in energy to the external (7*s*) shell to contribute materially to the chemical properties and to the valency: thus the characteristic valency seems to be 3 for actinium, 4 for thorium, and 5 for protoactinium; but, as Seaborg points out, the energy difference between a 5*f* and a 6*d* shell is not great and transitions or resonance may very easily occur.

The above suggestions as to the position of the new elements in the periodic system, and Seaborg's views on the electronic configuration of the actinide series, are set out in Tables 79 and 80. The principal point in connexion with the proposed electronic configuration appears to be to find a reason for the intensified similarity of the elements from uranium onwards, compared with the lesser degree of similarity of Elements 89 to 92, and possibly also for the progressive increase in the stability of the trivalent state in the transuranic series.

TABLE 79

<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>	<i>VIII</i>		
Y (39)	Zr (40)	Nb (41)	Mo (42)	Ma (43)	Ru (44)	Rh (45)	Pd (46)
(Rare earths)	Hf (72)	Ta (73)	W (74)	Re (75)	Os (76)	Ir (77)	Pt (78)
Ac (89)	Th (90)	Pa (91)	U (92)	Np (93)	Pu (94)	— (95)	— (96)

In the above tabulation, the separating line is intended to indicate that the new elements are not seventh- or eighth-group elements, like those vertically above them, but rather a separate group closely associated with uranium and possibly also with actinium.

TABLE 80

a. Standard Configuration

<i>Element</i>	<i>Z</i>		<i>O</i> 5 <i>f</i>	<i>P</i>			<i>Q</i> 7 <i>s</i>
				6 <i>s</i>	6 <i>p</i>	6 <i>d</i>	
Ra	88	Shells to 5 <i>d</i> all filled	—	2	6	—	2
Ac	89	„ „	—	2	6	1	2
Th	90	„ „	—	2	6	2	2
Pa	91	„ „	—	2	6	3	2
U	92	„ „	—	2	6	4	2

b. Suggested Modification (Seaborg)

Ac	89	Shells to 5 <i>d</i> all filled	—	2	6	1	2
Th	90	„ „	1	2	6	1	2
Pa	91	„ „	2	2	6	1	2
U	92	„ „	3	2	6	1	2
Np	93	„ „	4	2	6	1	2
Pu	94	„ „	5	2	6	1	2
—	95	„ „	6	2	6	1	2
—	96	„ „	7	2	6	1	2

NUCLEAR FISSION

Types of Nuclear Instability

The transition of an unstable nucleus to a more stable state may take place in at least two ways. In the first place, its initial structure may be such that stability can be reached by a minor configurational adjustment involving merely the ejection of a small mass particle or, in the case of radio-isomers, of γ -rays only. This type of transition, which occurs spontaneously at fixed rates which are evidently governed by probability laws, is classified as radioactivity and is, since the discovery of artificial radioactivity, known to take place in suitable nuclei throughout the range of the periodic system.

A further and more deeply seated type of instability appears ultimately to be reached if the number of particles associated to form a nucleus is progressively increased, in that nuclei of mass or atomic numbers beyond a limiting value are, as far as is known, incapable of existence. This factor was thought to limit the range of the natural elements to an upper value corresponding with an atomic number of 92; but, as already described, artificial elements having atomic numbers up to 96 have now been prepared, and very small concentrations of some of these may also occur naturally. The upper limit of mass appears to be just below 240.

This ultimate instability of a heavy nucleus as a whole can perhaps be understood qualitatively on grounds of the mutual repulsion of similarly charged nuclear protons, in that this repulsion, with increasing numbers of protons in a single nuclear complex, eventually becomes greater than the attractive forces present. A further factor may be the passage of the neutron-proton ratio into an unstable region, particularly if the limiting value of this ratio for stability changes with the atomic number, for, as will be seen on referring back to Fig. 1, both radioactive and stable isotopes of lower elements exist having neutron-proton ratios on each side of that (about 1.5) for uranium.

It is now known that nuclei bordering on general instability can change to a more stable state not only by the spontaneous ejection of relatively small mass particles, as in the radioactive type of stabilization, but also by fission processes in which the unstable nucleus as a whole is split into fragments of medium atomic weight. This type of process is induced artificially, above all by neutron bombardment; but spontaneous fission probably also takes place to some extent in nature (see p. 261).

Nuclear fission occurs only with the heaviest elements. The known isotopes of these, together with the abundances of the naturally occurring isotopes, are given in Table 81, some of the thorium and protoactinium isotopes which occur as intermediate products in the three natural radioactive series being omitted.

TABLE 81

<i>Element</i>	<i>Z</i>	<i>A</i>	<i>Nature of isotope</i>	<i>Percentage abundance</i>	<i>Half-life</i>	<i>Particles emitted</i>
Thorium	90	231	Artificial	—	24.5 hrs.	β^-
		232	Natural	100	1.6×10^{10} yrs.	α
		233	Artificial	—	26 min.	β^-
Protoactinium	91	231	Natural	?	3×10^4 yrs.	α
Uranium	92	234	Natural	0.006	2.7×10^6 yrs.	α
		235	Natural	0.71	7.1×10^8 yrs.	α
		237	Artificial	—	7 days	β^-
		238	Natural	99.28	4.56×10^9 yrs.	α
		239	Artificial	—	23 min.	β^-
Neptunium	93	237	Artificial	—	2.25×10^6 yrs.	α
		238	Artificial	—	2 days	β^-
		239	Artificial	—	2.3 days	β^-
Plutonium	94	238	Artificial	—	50 yrs.	α
		239	Artificial	—	2.4×10^4 yrs.	α

Discovery of Nuclear Fission

Fission has been studied in the greatest detail for uranium: indeed the clear recognition of this type of nuclear process dates from the establishment, by Hahn and Strassmann† early in 1939, of the true nature of the many products which can be obtained by irradiating uranium with neutrons‡ and which had up to then been regarded as transuranic elements. Hahn and Strassmann found among these products an isotope of barium ($Z = 56$), which was confirmed in a later paper§ in which the formation, from uranium, also of isotopes of strontium and ytterbium as well as of an inert gas and an alkali metal (probably Xe and Cs, or Kr and Rb) was described. These products, far from being transuranic elements, could only have been formed by the fission of the heavy uranium nucleus into fragments of medium atomic weight; and this explanation of their formation was advanced by Hahn and Strassmann. Similar products were obtained by the neutron bombardment of thorium. It may be noted that a radioactive rare earth element was also noticed among the supposedly transuranic elements by Curie and Savitch,|| but was not at the time regarded as a fission product.

Nature of the Fission Fragments

The identification of fission products, particularly from uranium, was subsequently pursued by a large number of workers. These products have been shown to fall into two mass groups, the lighter of which contains isotopes of all the elements from 35 to 43 inclusive (Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Ma), with atomic masses from slightly less than 90 to about 100, whereas the heavier group contains isotopes of Elements 51 to 57 (Sb, Te, I, Xe, Cs, Ba, La), the atomic masses ranging from slightly less than 130 to about 140. The diversity of the observed products is greatly increased by the radioactive character of most of the fragments; and it is certain that all the fission and subsequent products are not yet known. For a more detailed summary of the subject up to 1939–40, reference may be made to reviews by Frisch¶ and by Turner.†† A list, due to Frisch,

† O. Hahn and F. Strassmann, *Naturwiss.* 1939, 27, 11.

‡ E. Fermi, F. Amaldi, O. D'Agostino, F. Rasetti, and E. Segrè, *Proc. Roy. Soc.* 1934, A 146, 483.

§ O. Hahn and F. Strassmann, *Naturwiss.* 1939, 27, 89.

|| I. Curie and P. Savitch, *Compt. rend.* 1938, 206, 906, 1643.

¶ O. R. Frisch, *Ann. Reports Chem. Soc.* 1939, 36, 14; 1940, 37, 8.

†† L. A. Turner, *Rev. Mod. Phys.* 1940, 12, 1.

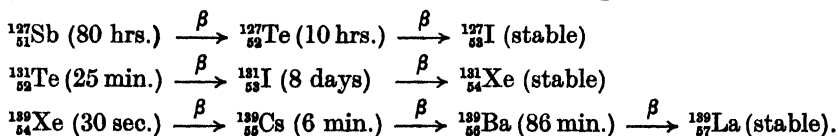
of uranium fission products known at the above period is given in Table 82. Those marked with an asterisk are also given by thorium. It will be seen that further disintegration usually takes place by β -decay.

TABLE 82

<i>Z</i>	<i>A</i>	<i>Element and course of subsequent decay</i>
<i>Lighter Group</i>		
35	—	Br (35–40 min.)
36	88	Kr* (3 hrs.) \rightarrow $_{37}\text{Rb}^*$ (17 min.)
38	—	Sr (7 min.)
	—	Sr (6 hrs.) \rightarrow $_{39}\text{Y}$ (3.5 hrs.)
	(89)	Sr* (54 days)
40	—	Zr (17 hrs.) \rightarrow $_{41}\text{Nb}$ (75 min.)
42	(99 or 101)	Mo* (67 hrs.) \rightarrow $_{43}\text{Ma}$ (6.6 hrs.)
<i>Heavier Group</i>		
51	—	Sb (5 min.) \rightarrow Te* (77 hrs.) \rightarrow I* (2.4 hrs.)
	(127)	Sb (80 hrs.) \rightarrow Te (10 hrs.)
	(129)	Sb (4.2 hrs.) \rightarrow Te (70 min.)
52	—	Te (43 min.) \rightarrow $_{53}\text{I}$ (54 min.)
	—	Te (60 min.) \rightarrow I (22 hrs.) \rightarrow Xe* (5.5 days)
	131	Te (30 hrs. and 25 min.; radio isomers) \rightarrow I (8 days)
53	—	I (6.6 hrs.) \rightarrow Xe* (9.4 hrs.)
54	139	Xe* (few sec.) \rightarrow $_{55}\text{Cs}^*$ (33 min.) \rightarrow Ba* (86 min.)
	140	Xe* (17 min.) \rightarrow Cs* (33 min.)
	—	Xe (short) \rightarrow Cs (short) \rightarrow Ba* (12 days)
56	—	Ba (14 min.) \rightarrow $_{57}\text{La}^*$ (3 hrs.) \rightarrow La* (40 hrs.)

It should be noted that although the gap from masurium to antimony ($Z = 43$ and 51) is definite for fission by slow or thermal neutrons, elements within this gap have been obtained by using very fast neutrons. Thus, $^{111}_{47}\text{Ag}$, $^{112}_{47}\text{Ag}$, $^{115}_{48}\text{Cd}$, $^{117}_{48}\text{Cd}$, and indium ($Z = 49$) isotopes formed by the radioactive decay of each of these cadmium isotopes have been found by Nishina and his co-workers.†

The state of published knowledge at the beginning of 1942 has been reviewed by Osgood,‡ who gives the most abundant fission products of uranium as Mo, Pd, Ag, Cd, Sb, Te, I, Cs, Ba, and La. Osgood quotes the following sequences as being typical of the many processes in which the mass numbers of the isotopes are known.



† Y. Nishina, T. Yasaki, H. Ezoe, K. Kimura, and M. Ikawa, *Nature*, 1940, **146**, 24.

‡ T. H. Osgood, *J. Appl. Phys.* 1942, **13**, 3.

It will be seen that some of these sequences also occur in Frisch's table, without, however, a detailed statement of the mass numbers, further that the half-life of the caesium isotope in the third sequence (leading to the 86-min. barium) differs from that given in the table.

The fission of protoactinium has been studied to a lesser degree than that of uranium and thorium, probably on account of its rarity. Like thorium, it is not split by slow neutrons.† The fission products fall into the same mass range as for uranium and thorium: e.g. rubidium ($Z = 37$) and caesium ($Z = 55$) have been recognized.

The free publication of work on nuclear fission had to be discontinued for security reasons in about 1942; but an outline of such of the main results of the very extensive Allied work as it has been considered advisable to make public has recently been given in an official monograph.‡

Fission by Particles other than Neutrons

Although neutron bombardment constitutes by far the most widely used method, fission may be induced by bombardment with other particles. For instance, Krishnan and Banks§ successfully employed 9-Mev. deuterons for the fission both of uranium and thorium, fragments which could be grouped into platinum, barium and lanthanum fractions being obtained in each case. High-energy (7 Mev.) protons from a cyclotron have also been used.|| Bombardment with high-energy γ -ray photons leads similarly to some fission both in uranium and in thorium.¶

Fission of Individual Isotopes

As will be seen from Table 81, natural thorium and probably also natural protoactinium are isotopically simple; and accordingly the possibility of differences in the susceptibility of isotopes to fission does not arise with these metals.

Of the three natural uranium isotopes, ^{234}U , ^{235}U , and ^{238}U , only ^{235}U can be split by neutrons of thermal energy.†† This was shown

† A. V. Grosse, E. T. Booth, and J. R. Dunning, *Phys. Rev.* 1939, **56**, 382.

‡ H. D. Smyth, *Atomic Energy*, United States Government Printing Office and H.M. Stationery Office, London, 1945.

§ R. S. Krishnan and T. E. Banks, *Nature*, 1940, **145**, 861.

|| G. Dessauer and E. M. Hafner, *Phys. Rev.* 1941, **59**, 680.

¶ E. O. Haxby, W. E. Shoupp, W. E. Stephens, and W. H. Wells, *ibid.* 1940, **58**, 92.

†† A. O. Nier, E. T. Booth, J. R. Dunning, and A. V. Grosse, *Phys. Rev.* 1940, **57**, 546, 748; K. H. Kingdon, H. C. Pollock, E. T. Booth, and J. R. Dunning, *ibid.*, p. 749; O. R. Frisch, *loc. cit.*

by the isotopic separation of uranium, by means of a mass spectrograph, and subjection of the separated isotopes to bombardment by thermal neutrons. The failure of the abundant ^{238}U isotope to undergo fission with slow neutrons has had far-reaching consequences in connexion with the utilization of natural uranium for the production of atomic (i.e. mass-conversion) energy by means of a chain reaction, since it has, for reasons which will be explained later, made necessary the large-scale separation of the less abundant isotope, ^{235}U . This separation has, however, been made on a very large scale, for instance by diffusion in the gaseous state of the hexafluoride made from the mixed uranium isotopes, the process being simplified by the isotopic simplicity of fluorine. For details, reference should be made to Smyth's monograph.

The first of the transuranic elements, neptunium, is of less interest, on account of the short half-life of its most easily accessible isotopes, than the second element, plutonium ($Z = 94$). Most of the experimental work has been done with ^{239}Pu , which can, as already discussed, be made from ^{238}U by neutron capture without fission followed by two successive β -decay steps and which, like ^{235}U , undergoes fission by slow neutrons. The utilization of plutonium in place of ^{235}U as a source of atomic energy brings with it the possibility of adopting a chemical rather than an isotopic separation, since plutonium is chemically different, at any rate to some degree, from uranium, whereas ^{235}U and ^{238}U are chemically identical.

Production of Secondary Neutrons

A highly important feature of nuclear fission is the emission of further or secondary neutrons as the result of a fission process induced by a primary or bombarding neutron. The discovery of this effect has had revolutionary consequences, since, if the number of secondary neutrons produced by the fissional capture of each primary neutron is greater than unity, the possibility exists (subject to considerations which are dealt with later) of a disintegration avalanche with progressive production of mass-annihilation energy. As the result of measurements by many workers,[†] it appears that an average of about three secondary neutrons are produced in each uranium fission.

It should be noted, further, that fission is also followed by the

[†] See the summaries by L. A. Turner, *Phys. Rev.* 1940, 57, 334, and by O. R. Frisch, *Ann. Reports Chem. Soc.* 1939, 36, 15; 1940, 37, 11, in which the original references are given.

emission of delayed neutrons, which may not be inherent in the fission process itself but may be emitted by the fission products.† In an experiment by Snell, Nedsel, and Ibsen‡ it was calculated that about 1 per cent. of the neutrons emitted by uranium fission are delayed by at least 0.01 sec. and that about 0.07 per cent. are delayed by as much as a minute.

FISSION AS A SOURCE OF ATOMIC ENERGY

This subject, which is the outstanding point of practical interest in connexion with atomic fission, can in spite of its revolutionary importance only be dealt with briefly and in a general manner, since the greater part of the recent work in this field is still unpublished. The basic principles were of course well known prior to the cessation of free publication; and the present short summary is limited to these and to such facts as have been made public in Smyth's official monograph or in articles§ which have recently been published, above all in the United States.

It can be calculated from the packing fraction curve that the disappearance of mass which results from the formation, from uranium, of fission products of the observed mass range should lead to the production of about 200 Mev. of energy per fission. This has been confirmed experimentally by the direct measurement of the heat produced by uranium fission. Thus, Henderson|| obtained a value of 175 Mev. with a probable error of 10 per cent. A figure of the same order has also been arrived at by other workers by determining the sum of the energies of the fission fragments. On the basis of these values, a gram of uranium should, by total fission, yield 5×10^7 kg.-cals. or slightly less than 6×10^4 kilowatt-hours; but it may be noted, in passing, that far greater energies even than this could be obtained if it were possible not only to split the heaviest elements but also to synthesize suitable simple nuclei from their constituent particles: thus the building up of a gram of helium (in which the nucleus has a mass defect of about 0.03 atomic mass units compared with the mass-sum of its constituent neutrons and protons) should release over three times the energy evolved by the fission of a gram of uranium.

† N. Bohr and J. A. Wheeler, *Phys. Rev.* 1939, **56**, 426.

‡ Quoted by H. D. Smyth, *Atomic Energy*, pp. 140-1.

§ See, for instance, L. S. Foster, *J. Chem. Education*, 1945, **22**, 619; M. L. Eidinoff, *ibid.* 1946, **23**, 60.

|| M. C. Henderson, *Phys. Rev.* 1939, **56**, 703.

In order to obtain a continuous supply of energy by the fission of uranium or of another heavy element it is essential that the reaction shall be self-propagating, namely that the secondary neutrons produced by each fission shall, on an average, cause at least one further fission. In this connexion it must be emphasized that although an average of about three secondary neutrons result from a fission, only a fraction of these will, by reason of the occurrence of alternative reactions, cause further fission.

The processes which may detract from the capacity of the secondary neutrons to carry on the reaction chain may be summarized† as follows:

- (i) non-fission capture by impurities;
- (ii) non-fission capture by uranium;
- (iii) escape from the uranium mass;

and, in any consideration of the self-propagation of fission, the number of secondary neutrons involved in all these non-fission processes must be subtracted from the gross number of secondary neutrons produced by each fission: for only if the ratio between this net number of secondary neutrons and the number of neutrons causing the fission is greater than unity will the fission chain proceed. The same relationship can obviously also be expressed in terms of the probabilities of the various non-fission and fission reactions.

It may be noted, further, that the originally high energies of the secondary neutrons may be reduced—by non-reactive inelastic collisions with uranium or impurity nuclei—to values which favour non-fission capture or even to values below these. The former would favour reactions (i) and (ii). The latter would favour fission only if the uranium isotope is split by low-energy neutrons, otherwise it would favour escape. Escape might thus result either by the failure of a neutron (primary or secondary) to make any direct nuclear hit or by the circumstance that all impacts made are at neutron speeds which are unfavourable for fissional or non-fissional capture.

Since the depression of the sum of the probabilities of non-fissional capture and escape to below a critical value is vital to the continuation of the fission chain, consideration may be given to each of these non-fission processes separately.

Reaction (i) may be suppressed in the initial stages of the chain by purifying the uranium; but the gradual accumulation of fission

† H. D. Smyth, *Atomic Energy*, p. 19.

products which will undergo nuclear reaction with the neutrons cannot be avoided. Nothing can be done to alter this; and this factor will at some stage eventually stop the chain. Accordingly only a part of the uranium will be available for the production of energy unless the fission products are removed by periodical purification. There can of course be no question of this if the uranium is involved in an explosive reaction; but this necessity for periodical purification certainly arises if fission is to be used as a means of producing energy at a controlled rate.

The degree of influence of the second type of reaction (non-fissional capture of secondary neutrons by uranium) depends not only on the width and position of the neutron energy range in which this type of resonance capture takes place but also on the neutron energies for which fission is most probable. If, as is the case with ^{235}U , the energy range for resonance capture is not too large, and if it lies at an intermediate stage between the original high energy value of the fast secondary neutrons and the low or thermal neutron energies at which fission is most probable, fission will be favoured—and the probability of non-fission capture depressed—by quickly lowering the neutron energies to thermal values in such a way as to pass through the non-fission capture region as rapidly as possible. This can be done by using a so-called moderator such as graphite or a deuterium compound (heavy water), both of which are more efficient in reducing neutron speeds than the compounds of ordinary hydrogen (water or hydrocarbons) which were widely used in earlier nuclear work not connected with fission. The use of beryllium has also been suggested. It is found advantageous to introduce the moderator in the form of pieces of moderate size rather than to mix this intimately with the uranium: thus effective self-sustaining energy ‘piles’ have been constructed by interspersing spheres or other shapes of uranium with pieces of graphite, these components being arranged in a definite geometrical pattern.

Process (iii), namely the escape of neutrons from the system, is a surface effect, the probability of which will be proportional to the area over which this escape can take place. For instance, if the uranium is in the form of a sphere, the rate of escape will be a function of r^2 . Fission, on the other hand—like non-fission capture either by uranium or by impurities—is a volume effect and proportional to r^3 . Consequently the ratio of escape to fission will diminish as

the size of the sphere is increased; and, if the losses of neutrons by non-fission capture are not too great, a critical size will exist beyond which the escape factor becomes too small to play a significant role in stopping the chain.

Use of Individual Uranium Isotopes

As has already been mentioned, ^{238}U and ^{235}U differ from the standpoint of fission, in that while the former is split, above all, by fast neutrons, the fission of ^{235}U is most probable for thermal neutrons and less probable for neutrons of higher energies. This may be expressed in other words by saying (see p. 227) that ^{238}U has an appreciable fissional cross-section for fast neutrons only, and that ^{235}U has a large cross-section for thermal neutrons. In addition, ^{238}U possesses a large cross-section for non-fission capture, the capture process being facilitated by inelastic non-reactive collisions in the course of which the neutron energies pass through the resonance region and, below this, to thermal values at which fission does not occur in ^{238}U . All these factors make natural uranium, which contains over 99 per cent. of ^{238}U , unsuitable for use in atomic energy piles.

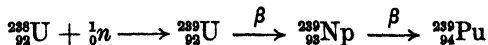
The rarer isotope, ^{235}U , does not suffer from these disadvantages. It has, firstly, a higher fissional cross-section for thermal neutrons than ^{238}U has for high-energy neutrons, secondly, a lower cross-section for non-fission capture, and thirdly, it is also split by fast neutrons, although its cross-section for these is lower than for thermal neutrons. For these reasons, elaborate steps have been taken to separate pure or at least enriched ^{235}U by the gaseous diffusion of the fluoride or by other methods, for details of which reference should be made to Smyth's monograph.

It may be noted that, in addition to employing an energy pile consisting of pieces of ^{235}U interspersed with pieces of a moderator such as graphite, the construction of a self-supporting pile based on fast rather than slow neutron fission and containing no moderator is by no means out of the question with ^{235}U , in spite of its lower cross-section for fast, compared with slow, neutron fission.

Use of Plutonium

Although the more abundant uranium isotope, ^{238}U , is unsuitable in itself for the continuous production of energy, it may, as has

already been discussed on p. 260, be used as a source of Element 94, the process



being greatly facilitated by the large cross-section of ${}^{238}\text{U}$ for this resonance capture of neutrons without fission. This reaction enables natural uranium to be used indirectly as a source of energy, the capture reaction being allowed to proceed to a convenient extent, after which the reaction mass is worked up for plutonium. The separation of plutonium from the residual uranium should be possible by chemical means since plutonium and uranium, although closely related, are different elements, a chemical separation being thus substituted for the difficult isotopic separation of ${}^{235}\text{U}$ from ${}^{238}\text{U}$; but in practice the operation is complicated by the presence of fission products and by the close similarity of plutonium to uranium. In spite of these difficulties, plutonium has been successfully prepared on a large scale. It is split by thermal neutrons and appears to constitute an effective alternative to ${}^{235}\text{U}$ in energy piles. The chief point of interest in connexion with plutonium is of course that its use would allow substantially the whole of natural uranium (subject to working-up losses) to be utilized for energy production in place of the very small percentage of uranium represented by its ${}^{235}\text{U}$ content.

TABULAR APPENDIX

TABLE I

Electron Configurations of the Elements†

<i>Z</i>	<i>K</i> 1 <i>s</i>	<i>L</i> 2 <i>s</i> 2 <i>p</i>	<i>M</i> 3 <i>s</i> 3 <i>p</i> 3 <i>d</i>	<i>N</i> 4 <i>s</i> 4 <i>p</i> 4 <i>d</i> 4 <i>f</i>	<i>O</i> 5 <i>s</i> 5 <i>p</i> 5 <i>d</i>	<i>P</i> 6 <i>s</i> 6 <i>p</i> 6 <i>d</i>	<i>Q</i> 7 <i>s</i>
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 1					
6 C	2	2 2					
7 N	2	2 3					
8 O	2	2 4					
9 F	2	2 5					
10 Ne	2	2 6					
11 Na	Orbits to 2 <i>p</i> filled		1				
12 Mg			2				
13 Al			2 1				
14 Si			2 2				
15 P			2 3				
16 S			2 4				
17 Cl			2 5				
18 A			2 6				
19 K	Orbits to 3 <i>p</i> filled			1			
20 Ca				2			
21 Sc			1*	2			
22 Ti			2*	2			
23 V			3*	2			
24 Cr			5*	1			
25 Mn			5	2			
26 Fe			6*	2			
27 Co			7*	2			
28 Ni			8*	2			
29 Cu	Orbits to 3 <i>d</i> filled		10*	1			
30 Zn				2			
31 Ga				2 1			
32 Ge				2 2			
33 As				2 3			
34 Se				2 4			
35 Br				2 5			
36 Kr				2 6			
37 Rb	Orbits to 4 <i>p</i> filled				1		
38 Sr					2		
39 Y				1*	2		
40 Zr				2*	2		
41 Nb				4*	1		
42 Mo				5*	1		
43 Ma				6*	1		
44 Ru				7*	1		
45 Rh				8*	1		
46 Pd				10*			

† Cases in which the new electron, in the ascending *Z* series, is added to an internal orbit are marked with an asterisk.

TABLE I (continued)

Z	K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d	P 6s 6p 6d	Q 7s
47 Ag	Orbits to 4d filled				1		
48 Cd					2		
49 In					2 1		
50 Sn					2 2		
51 Sb					2 3		
52 Te					2 4		
53 I					2 5		
54 Xe					2 6		
55 Cs					2 6	1	
56 Ba					2 6	2	
57 La					2 6 1*	2	
58 Ce					1* 2 6 1	2	
59 Pr					2* 2 6 1	2	
60 Nd					3* 2 6 1	2	
61 Il					4* 2 6 1	2	
62 Sm					5* 2 6 1	2	
63 Eu					6* 2 6 1	2	
64 Gd					7* 2 6 1	2	
65 Tb					8* 2 6 1	2	
66 Dy					9* 2 6 1	2	
67 Ho					10* 2 6 1	2	
68 Er					11* 2 6 1	2	
69 Tm					12* 2 6 1	2	
70 Yb					13* 2 6 1	2	
71 Lu					14* 2 6 1	2	
72 Hf	Orbits to 5p filled				2*	2	
73 Ta					3*	2	
74 W					4*	2	
75 Re					5*	2	
76 Os					6*	2	
77 Ir					9		
78 Pt					9	1	
79 Au	Orbits to 5d filled				10*	1	
80 Hg						2	
81 Tl						2 1	
82 Pb						2 2	
83 Bi						2 3	
84 Po						2 4	
85 —						2 5	
86 Rn						2 6	
87 —	Orbits to 6p filled						1
88 Ra							2
89 Ac						1*	2
90 Th						2*	2
91 Pa						3*	2
92 U						4*	2

TABLE II

Abundances, Isotopic Weights, and Packing Fractions of the Naturally Occurring Isotopes†

<i>Z</i>	<i>Element</i>	<i>A</i>	<i>Percentage abundance</i>	<i>Isotopic weight</i> (¹⁶ O = 16)	<i>Packing fraction</i> × 10 ⁴
1	H	1	99.98	1.00812	+81.2
		2	0.02	2.01471	+73.55
2	He	3	10 ⁻⁶ ?	3.0171	+57.0
		4	100	4.00391	+9.77
3	Li	6	7.9	6.0169	+28.2
		7	92.1	7.0182	+26.0
4	Be	9	100	9.0155	+17.2
5	B	10	18.4	10.0161	+16.1
		11	81.6	11.0129	+11.7
6	C	12	98.9	12.0040	+3.32
		13	1.1	13.0076	+5.85
7	N	14	99.62	14.0073	+5.28
		15	0.38	15.0049	+3.27
8	O	16	99.76	16.0000	0
		17	0.04	17.0045	+2.65
		18	0.20	18.0037	+2.06
9	F	19	100	19.0045	+2.36
10	Ne	20	90.00	19.9988	-0.60
		21	0.27	20.9997	-0.14
		22	9.73	21.9986	-0.64
11	Na	23	100	22.9961	-1.65
12	Mg	24	77.4	23.9924	-3.17
		25	11.5	24.9938	-2.48
		26	11.1	25.9898	-3.92
13	Al	27	100	26.9899	-3.74
14	Si	28	89.6	27.9863	-4.90
		29	6.2	28.9866	-4.62
		30	4.2	29.9832	-5.60
15	P	31	100	30.9836	-5.30
16	S	32	95.0	31.9283	-5.53
		33	0.74	—	—
		34	4.2	33.978	-6.47
		36	0.016	—	—
17	Cl	35	75.4	34.9800	-5.71
		37	24.6	36.9975	-6.10
18	A	36	0.307	35.9780	-6.10
		38	0.061	37.974	-6.84
		40	99.632	39.9754	-6.15

† Based on F. W. Aston, *Proc. Roy. Soc.* 1937, A 163, 391; A. J. Dempster, *Phys. Rev.* 1938, 53, 74, 869; O. Hahn, *Ber.* 1938, 71, 1; G. T. Seaborg, *Chem. Reviews*, 1940, 27, 211.

TABLE II (continued)

The remainder of the table is given in a condensed form, since the individual atomic weights of many of the isotopes of the heavier elements are less accurately known. Dempster's values for the packing fractions, f , from which these isotopic weights can readily be calculated, are marked (D). Aston's values are denoted by (A). The calculated packing fractions are due to Hahn. The isotopes marked with an asterisk are naturally radioactive.

Z	Element	A	Abundance	$f \times 10^4$	Z	Element	A	Abundance	$f \times 10^4$
19	K	39	93.30		31	Ga	69	61.2	
		40*	0.01	-7 (est.)			71	38.8	-6.72 (D)
		41	6.6						
20	Ca	40	96.96		32	Ge	70	21.2	
		42	0.64				72	27.3	
		43	0.15	-7.2 (est.)			73	7.9	-7.7 (est.)
		44	2.06				74	37.1	
		46	0.0033				76	6.5	
		48	0.19		33	As	75	100	-8.8 (A)
21	Sc	45	100	-7 (est.)	34	Se	74	0.9	
22	Ti	46	7.95				76	9.5	
		47	7.75				77	8.3	
		48	73.45	-7.2 (D)			78	24.0	-8.0 (A)
		49	5.51				80	48.0	-7.3 (A)
		50	5.34				82	9.3	
23	V	51	100	-9 (est.)	35	Br	79	50.6	-9.0 (A)
24	Cr	50	4.49				81	49.4	-8.6 (A)
		52	83.77	-10.0 (A)	36	Kr	78	0.35	-7.30 (A)
		53	9.43				80	2.01	
		54	2.30				82	11.53	-7.70 (A)
							83	11.53	
25	Mn	55	100	-10 (est.)			84	57.10	-7.60 (A)
							86	17.47	-7.40 (A)
26	Fe	54	6.04	-7.4 (D)	37	Rb	85	72.3	-8.2 (est.)
		56	91.57	-7.0 (D)			87*	27.7	
		57	2.11		38	Sr	84	0.56	
		58	0.28	-10 (est.)			86	9.86	-8.2 (est.)
27	Co	57	0.17				87	7.02	
		59	99.83	-10 (est.)			88	82.56	
28	Ni	58	68.0	-10.0 (A)	39	Y	89	100	-9.1 (est.)
		60	27.2		40	Zr	90	48	
		61	0.1				91	11.5	
		62	3.8				92	22	-7 (est.)
		64	0.9				94	17	
29	Cu	63	68	-6.9 (D)			96	1.5	
		65	32	-10 (est.)	41	Nb	93	100	-8 (A)
30	Zn	64	50.9	-6.9 (D)	42	Mo	92	15.5	
		66	27.3	-7.4 (D)			94	8.7	
		67	3.9				95	16.3	
		68	17.4	-9.9 (est.)			96	16.8	
		70	0.5				97	8.7	
							98	25.4	-5.5 (A)
							100	8.6	-5.5 (A)

TABLE II (continued)

<i>Z</i>	<i>Element</i>	<i>A</i>	<i>Abundance</i>	<i>f</i> × 10 ⁴	<i>Z</i>	<i>Element</i>	<i>A</i>	<i>Abundance</i>	<i>f</i> × 10 ⁴
44	Ru	96	5		54	Xe	124	0.094	
		98	—				126	0.088	
		99	12				128	1.90	
		100	14	— 6 (est.)			129	26.23	— 4.46 (A)
		101	22				130	4.07	
		102	30				131	21.17	
		104	17				132	26.96	— 4.4 (A)
45	Rh	101	0.08	— 5.7 (est.)			134	10.54	
		103	99.92				136	8.95	
46	Pd	102	0.8		55	Cs	133	100	— 5 (A)
		104	9.3		56	Ba	130	0.101	
		105	22.6				132	0.097	
		106	27.2	— 5.35 (D)			134	2.42	
		108	26.8				135	6.59	
		110	13.5				136	7.81	
47	Ag	107	52.5	— 4.95 (D)			137	11.32	
		109	47.5				138	71.66	— 6.1 (A)
48	Cd	106	1.4		72	Hf	(Rare earths omitted)		
		108	1.0				172?	< 0.1	
		110	12.8				174	0.3	
		111	13.0	— 6.5 (est.)			176	5	
		112	24.2				177	19	— 3 (est.)
		113	12.3				178	28	
		114	28.0				179	18	
		116	7.3				180	30	
49	In	113	4.5	— 7.4 (est.)	73	Ta	181	100	— 4 (A)
		115	95.5		74	W	180	0.2	
							182	22.6	
50	Sn	112	1.1				183	17.3	+ 1.8 (D)
		114	0.8				184	30.1	
		115	0.4				186	29.8	
		116	15.5		75	Re	185	38.2	
		117	9.1	— 5.0 (D)			187	61.8	— 1 (A)
		118	22.5		76	Os	184	0.018	
		119	9.8	— 5.2 (D)			186	1.59	
		120	28.5				187	1.64	
		122	5.5				188	13.3	
		124	6.8	— 4.5 (D)			189	16.1	
51	Sb	121	56	— 6.3 (est.)			190	26.4	— 1 (A)
		44					192	41.0	— 1 (A)
52	Te	120	< 0.1		77	Ir	191	38.5	0 (est.)
		122	2.9		78	Pt	193	61.5	
		123	1.6				192	0.8	
		124	4.5				194	30.2	
		125	6.0				195	35.3	+ 2.03 (D)
		126	19.9	— 5 (A)			196	26.6	
		128	32.8	— 5 (A)			198	7.2	
		130	33.1						
53	I	127	100	— 5.3 (A)	79	Au	197	100	+ 2.0 (D)

TABLE II (continued)

<i>Z</i>	<i>Element</i>	<i>A</i>	<i>Abundance</i>	$f \times 10^4$	<i>Z</i>	<i>Element</i>	<i>A</i>	<i>Abundance</i>	$f \times 10^4$		
80	Hg	196	0.15	$+1.4$ (A)	83	Bi	209	100	$+2$ (est.)		
		198	10.1		90	Th	232*	100	$+3$ (est.)		
		199	17.0								
		200	23.3		91	Pa	231*	—	—		
		201	13.2								
		202	29.6		92	U	234*	0.006	$+5.56$ (D)		
		204	6.7				235*	0.71			
81	Tl	203	29.1	$+1.8$ (A)			238*	99.28			
		205	70.9								
82	Pb	204	1.48	$+2.3$ (D)							
		206	23.59								
		207	22.64								
		208	52.29								

TABLE III

Atomic Weights of the Natural Elements
(Chemical Scale)

<i>Element</i>	<i>Symbol</i>	<i>Atomic weight</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic weight</i>
Aluminium	Al	26.97	Neon	Ne	20.183
Antimony	Sb	121.76	Nickel	Ni	58.69
Argon	A	39.944	Niobium (or Columbium)	Nb (Cb)	92.91
Arsenic	As	74.91	Nitrogen	N	14.008
Barium	Ba	137.36	Osmium	Os	190.2
Beryllium	Be	9.02	Oxygen	O	16.0000
Bismuth	Bi	209.00	Palladium	Pd	106.7
Boron	B	10.82	Phosphorus	P	30.98
Bromine	Br	79.916	Platinum	Pt	195.23
Cadmium	Cd	112.41	Potassium	K	39.096
Caesium	Cs	132.91	Praseodymium	Pr	140.92
Calcium	Ca	40.08	Protoactinium	Pa	231
Carbon	C	12.010	Radium	Ra	226.05
Cerium	Ce	140.13	Radon	Rn	222
Chlorine	Cl	35.457	Rhenium	Re	186.31
Chromium	Cr	52.01	Rhodium	Rh	102.91
Cobalt	Co	58.94	Rubidium	Rb	85.48
Copper	Cu	63.57	Ruthenium	Ru	101.7
Dysprosium	Dy	162.46	Samarium	Sm	150.43
Erbium	Er	167.2	Scandium	Sc	45.10
Europium	Eu	152.0	Selenium	Se	78.96
Fluorine	F	19.00	Silicon	Si	28.06
Gadolinium	Gd	156.9	Silver	Ag	107.880
Gallium	Ga	69.72	Sodium	Na	22.997
Germanium	Ge	72.60	Strontium	Sr	87.63
Gold	Au	197.2	Sulphur	S	32.06
Hafnium	Hf	178.6	Tantalum	Ta	180.88
Helium	He	4.003	Tellurium	Te	127.61
Holmium	Ho	163.5	Terbium	Tb	159.2
Hydrogen	H	1.0080	Thallium	Tl	204.39
Indium	In	114.76	Thorium	Th	232.12
Iodine	I	126.92	Thulium	Tm	169.4
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.85	Titanium	Ti	47.90
Krypton	Kr	83.7	Tungsten	W	183.92
Lanthanum	La	138.92	Uranium	U	238.07
Lead	Pb	207.21	Vanadium	V	50.95
Lithium	Li	6.940	Xenon	Xe	131.3
Lutecium	Lu	174.99	Ytterbium	Yb	173.04
Magnesium	Mg	24.32	Yttrium	Y	88.92
Manganese	Mn	54.93	Zinc	Zn	65.38
Mercury	Hg	200.61	Zirconium	Zr	91.22
Molybdenum	Mo	95.95			
Neodymium	Nd	144.27			

TABLE IV
Periodic System of the Elements

O	I		II		III		IV		V		VI		VII		VIII	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b		
	H 1															
He 2	Li 3		Be 4		B 5		C 6		N 7		O 8		F 9			
Ne 10	Na 11		Mg 12		Al 13		Si 14		P 15		S 16		Cl 17			
A 18	K 19		Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25		Fe 26	Co 27
		Cu 29		Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35		Ni 28
Kr 36	Rb 37		Sr 38		Y 39		Zr 40		Nb 41		Mo 42		Ma 43		Ru 44	Rh 45
		Ag 47		Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53		Pd 46
Xe 54	Cs 55		Ba 56		Rare earths 57-71		Hf 72		Ta 73		W 74		Re 75		Os 76	Ir 77
																Pt 78
		Au 79		Hg 80		Tl 81		Pb 82		Bi 83		Po 84		— 85		
Rn 86	— 87		Ra 88		Ac 89		Th 90		Pa 91		U 92					

TABLE V

*Atomic Radii†**a. Normal Covalent Radii*

Element	Effective radius, in <i>A</i>		
	Single-bond	Double-bond	Triple-bond
H	0.30 to 0.37	—	—
Li	1.34	—	—
Na	1.54	—	—
K	1.96	—	—
Rb	2.11	—	—
Cs	2.26	—	—
B	0.89	0.76	0.68
C	0.77	0.67	0.60
Si	1.17	1.07	1.00
Ge	1.22	1.12	—
Sn	1.40	—	—
Pb	1.46	—	—
N	0.74	0.61	0.55
P	1.10	1.00	0.93
As	1.21	—	—
Sb	1.41	—	—
Bi	1.51	—	—
O	0.66	0.57	—
S	1.04	0.95	—
Se	1.17	1.08	—
Te	1.37	1.28	—
F	0.64	0.55	—
Cl	0.99	0.90	—
Br	1.14	1.05	—
I	1.33	1.24	—

For tables of tetrahedral (sp^3), octahedral (d^2sp^3), and square (dsp^2) radii, see L. Pauling and M. L. Huggins, *Z. Krist.* 1934, 87, 205, also L. Pauling, *Nature of the Chemical Bond*, pp. 165–73. The tetrahedral radii of the carbon group are, of course, the normal radii.

b. Ionic-Crystal Radii

The values of these are less definite than those of the covalent radii.

† Based on values given by M. L. Huggins, *Phys. Rev.* 1926, 28, 1086; V. M. Goldschmidt, 'Geochemische Verteilungsgesetze der Elemente', *Skrifter d. Norske Videnskaps-Akad. Oslo. I. Matem.-Naturvid. Klasse*, 1926; *Trans. Faraday Soc.* 1929, 25, 253; L. Pauling, *J. Amer. Chem. Soc.* 1927, 49, 765; L. Pauling and M. L. Huggins, loc. cit.; V. Schomaker and M. L. Huggins, *J. Amer. Chem. Soc.* 1941, 63, 37.

TABLE V (continued)

I			II		III		IV	
a	Li ⁺	0.60	Be ²⁺	0.31	—		—	
	Na ⁺	0.95	Mg ²⁺	0.65	Al ³⁺	0.50	—	
	K ⁺	1.33	Ca ²⁺	0.99	Sc ³⁺	0.81	Ti ⁴⁺	0.68
	Rb ⁺	1.48	Sr ²⁺	1.13	Y ³⁺	0.93	Zr ⁴⁺	0.80
	Cs ⁺	1.69	Ba ²⁺	1.35	La ³⁺	1.15	Ce ⁴⁺	1.01
b	Cu ⁺	0.96	Zn ²⁺	0.74	Ga ³⁺	0.62	Ge ⁴⁺	0.53
	Cu ²⁺	1.01						
	Ag ⁺	1.26	Cd ²⁺	0.97	In ³⁺	0.81	Sn ⁴⁺	0.71
	Au ⁺	1.37	Hg ²⁺	1.10	Tl ⁺	1.44	Pb ²⁺	1.21
					Tl ³⁺	0.95	Pb ⁴⁺	0.84

V			VI		VII		VIII (Iron group only)	
a	V ³⁺	0.66	Cr ³⁺	0.64	Mn ²⁺	0.80	Fe ³⁺	0.75
	V ⁵⁺	0.59	Cr ⁶⁺	0.52	Mn ⁷⁺	0.46	Fe ²⁺	0.60
	Nb ⁵⁺	0.70	Mo ⁶⁺	0.62	—		Co ²⁺	0.72
b	N ³⁻	1.71	O ²⁻	1.40	F ⁻	1.36	Ni ²⁺	
	P ³⁻	2.12	S ²⁻	1.84	Cl ⁻	1.81		
	As ³⁻	2.22	Se ²⁻	1.98	Br ⁻	1.95		
	Sb ³⁻	2.45	Te ²⁻	2.21	I ⁻	2.16		
	Sb ⁵⁺	0.62						
	Bi ⁵⁺	0.74						

TABLE VI†

*Miscellaneous Data**a. Masses of Particles*

Particle	Mass, in atomic units		Mass, in grams
	Physical scale (¹⁶ O = 16)	Chemical scale (O = 16)	
Electron	0.0005486	0.0005485	9.1066×10^{-28}
Neutron	1.00893	1.00865	1.67472×10^{-24}
Proton (¹ H - e ⁻)	1.00758	1.00730	1.67248×10^{-24}
Neutral ¹ H atom	1.00813	1.00785	1.67339×10^{-24}
Deuteron (² D - e ⁻)	2.01418	2.01363	3.34334×10^{-24}
Neutral ² D atom	2.01473	2.01418	3.34425×10^{-24}
α-Particle	4.00279	4.00170	6.6442×10^{-24}
Neutral ⁴ He atom	4.00389	4.00280	6.6460×10^{-24}

Mass, in grams, of atom of unit atomic wt. (chemical scale) = 1.66035×10^{-24} .

Mass, in grams, of atom of unit atomic wt. (physical scale) = 1.65990×10^{-24} .

Factor for conversion of chemical to physical at. wts. = 1.000272.

† Based mainly on the compilation of most probable values for physical constants by R. T. Birge, *Rev. Mod. Physics*, 1941, 13, 234; *J. Chem. Soc.* 1946, 219.

b. Energy-Mass Conversion Data

1 gram (mass) is equivalent to 8.9866×10^{20} ergs (energy)
 $= 5.6095 \times 10^{26}$ Mev. (energy)
 $= 2.50 \times 10^7$ kw.-hrs.

1 atomic mass unit (chemical scale) is equivalent to 9.3127×10^3 Mev.

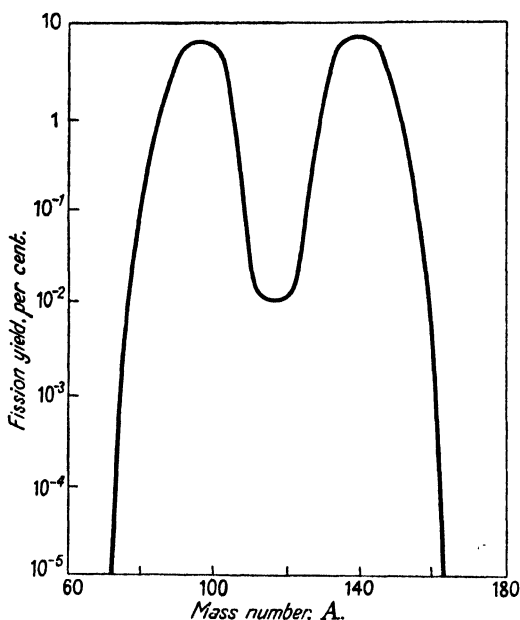
1 atomic mass unit (physical scale) is equivalent to 9.3111×10^3 Mev.

1 atomic mass unit is equivalent to 4.14×10^{-17} kw.-hrs.

1 Mev. is equivalent to 1.0738×10^{-3} atomic mass units.

c. Mass-distribution of Uranium Fission Products†

The percentage yields of the various elements formed as fission products, when plotted on a logarithmic scale as a function of the mass numbers of the products on a linear scale, follow a curve of the form given below:

*d. Miscellaneous Constants*

$c = (2.99776 \pm 0.00004) \times 10^{10}$ cm./sec.

h (Planck's constant) $= (6.624 \pm 0.002) \times 10^{-27}$ erg-sec.

N (Avogadro number) $= (6.023 \pm 0.001) \times 10^{23}$.

\AA (Angstrom unit) $= 10^{-8}$ cm.; $1 \mu = 10^{-6}$ cm.; $1 \mu\mu = 10^{-7}$ cm.

1 electron-volt $= (1.60203 \pm 0.0034) \times 10^{-12}$ erg.

1 electron-volt per molecule $= 23053$ cal. per g.-mol.

† See the comprehensive survey of fission products (*J. Amer. Chem. Soc.* 1946, 68, 2411) prepared by J. M. Siegel and issued by the Plutonium Project.

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